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ELEMENTARY QUANTITATIVE CHEMISTRY, A LABORATORY TEXT.
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A MANUAL WAS PRODUCED CONTAINING LABORATORY PROCEDURES FOR A ONE-SEMESTER COURSE IN ELEMENTARY QUANTITATIVE CHEMISTRY ON A COLLEGE FRESHMAN LEVEL. MATERIALS AND TOPICS WERE EXAMINED AND CHOSEN AS TO DESIRABILITY, PRACTICALITY, AND EDUCATIONAL VALUE. OPTIONAL EXPERIMENTS WERE ALSO INCLUDED. THE LABORATORY PROCEDURES WERE TESTED ON SOPHOMORES AND ON FRESHMEN. NO APPRECIABLE DIFFERENCE WAS DETECTED IN THE OVERALL PERFORMANCE OF THE TWO GROUPS. A COMPARISON OF THE LABORATORY RESULTS UNDER THE OLD AND NEW PROCEDURES REVEALED THAT GRADES WITH THE NEW PROCEDURES AVERAGED 6 PERCENT HIGHER THAN GRADES OBTAINED WITH THE OLD PROCEDURES. IT WAS CONCLUDED THAT QUANTITATIVE CHEMISTRY IS A SUITABLE COURSE FOR THE FRESHMAN COLLEGE LEVEL, AND PRESENTATION OF THIS COURSE SHOULD NOT BE PUT OFF UNTIL THE SOPHOMORE YEAR. THE AUTHORS CAUTIONED THAT THIS LABORATORY COURSE WOULD NOT SERVE AS A SUBSTITUTE FOR ADVANCED COURSES IN INSTRUMENTAL ANALYSIS WHICH ARE USUALLY OFFERED DURING THE JUNIOR OR SENIOR YEAR FOR CHEMISTRY MAJORS. (GD)

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ELEMENTARY QUANTITATIVE CHEMISTRY, (5-8337)

A laboratory text

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PREFACE

This manual provides laboratory procedures for a one-semester course in elementary quantitative chemistry on a freshman level. In recent years the high school training in chemistry of entering college freshmen has improved significantly. Much of the material traditionally included in introductory college chemistry courses is being offered in high schools, and our procedures seek to take advantage of the trend. It now appears feasible to offer instruction in precise quantitative analysis during the second semester of the freshman year. This statement does not imply that the procedures are necessarily elementary; indeed, the experiments may provide a challenge to more advanced students. The authors simply recognize the fact that many high schools and preparatory schools are doing such a good job in the teaching of general chemistry that the college freshman today is prepared to undertake more exacting work.

The rapid strides in chemical instrumentation are having a profound effect upon the methods of chemical analysis. Such instruments as electrical one-pan balances, pH meters, spectrophotometers, and calculating machines are becoming standard equipment, not only in chemical research but also in diagnostic medicine and in the chemical industry. The majority of the Washington and Lee freshmen chemistry students are either pre-medical students or science majors. Therefore, the course in quantitative chemistry includes considerable use of instrumentation, so as to familiarize these students with fundamental equipment which may be of importance to them in their future professions. However, it is to be understood that the present laboratory course will not serve as a substitute for advanced courses in instrumental analysis, which are usually offered during the junior or senior year for chemistry majors.

Our problem has been the development of a laboratory program in quantitative chemistry, suitable for freshman pre-medical and other science students, retaining the emphasis upon precise laboratory technique usually associated with sophomore quantitative analysis courses, but providing training in the use of essential instruments of analytical chemistry. One particular aspect of this problem is that of integrating the use of instruments with classical quantitative techniques.

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INTRODUCTION

Analytical chemistry consists of two major divisions, qualitative analysis and quantitative analysis. The laboratory procedures of qualitative analysis are designed for identifying and determining the approximate amounts of the constituents present in a substance, whereas the procedures of quantitative analysis are concerned with determining the exact amounts of constituents present. A complete analysis of a sample must include both qualitative and quantitative determinations. However, the qualitative analysis must precede the quantitative, since the former serves as a basis for selecting methods for the latter.

The Methods of Quantitative Chemistry. Quantitative methods may be conveniently subdivided into four general divisions: gravimetric, volumetric, colorimetric, and electrical methods. However, such a classification is more arbitrary than accurate since, frequently, an analytical procedure may employ more than one method in arriving at the percentage composition of a substance. It seems pertinent to summarize the nature of these quantitative measurements.

Gravimetric Methods. A gravimetric analysis is one based entirely upon weight. In such a procedure the original substance is weighed, and from it the constituent to be determined is isolated and also weighed. From the two weights the amount of the desired constituent is calculated.

Volumetric Methods. A volumetric determination is made by measuring the volume of a standard reagent reacting with the desired constituent in a definite chemical reaction. The amount of the constituent may be obtained from the weight of the original sample and the milliequivalents of the standard solution used in the titration.

Colorimetric Methods. The substance to be determined is converted to a compound which imparts a distinctive color to its solution. The intensity of the color of an unknown solution is compared with standard solutions containing known amounts of the colored compound. Such a comparison may provide an estimation of percentage composition.

Electrical Methods. Among these many methods can be listed the measurements of certain basic electrical properties such as potential, conductance, quantity, and capacitance. A correlation of these physical measurements with concentrations, for knowns and unknowns, provides a means for quantitative evaluations.

The Objectives of Quantitative Chemistry. The laboratory procedures in quantitative chemistry provide experiences and situations which have disciplinal, educational, and practical values in the training of a student. An elaboration of these values is as follows:

Disciplinal Values. In the analysis of a substance a student strives to obtain results which are near to percentages that are known only to the instructor. In seeking a high degree of accuracy certain personal qualities are essential:

(1) The student must have a sense of objective honesty in the evaluation of laboratory measurements.

(2) He must be able to follow directions carefully and intelligently, and to make accurate observations and readings.

(3) He must acquire neat and precise working habits, and always record laboratory data in a systematic form in a suitable notebook.

Educational Values. Very few students who complete a course in quantitative chemistry will ever enter a profession which requires routine analytical determinations. However, the educational values within the study are fully as important as any other values which may be attributed to the course. Among the educational values may be listed the following:

(1) The student is given an opportunity to use certain aspects of applied mathematics.

(2) He supplements and expands his knowledge of some basic principles of analytical chemistry.

(3) He becomes familiar with the literature of analytical chemistry.

Practical Values. Quantitative chemistry is usually the only course in a chemistry curriculum that has the attainment of precise and accurate results as a primary objective.

(1) To attain accurate results a student must acquire manipulative

ability and reasonable speed in the handling of chemical equipment.

(2) He must appreciate the limitations of the methods and equipment he uses, and the magnitude of possible errors which may be involved.

(3) He must be able to make rapid calculations from analytical observations to a precision warranted by the data included.

Finally, one of the most outstanding rewards of a course in quantitative chemistry for a student is the attainment of an instilled confidence in his laboratory skills. This confidence permits the proper approach to almost any type of laboratory problem; it is quite evident in advanced courses, in research, and in the problems which may be faced in professional and industrial laboratories.

Chapter 1

GENERAL LABORATORY DIRECTIONS

BEGINNING THE LABORATORY WORK

1·1 Planning and Schedule. The laboratory work in analytical chemistry is usually planned so that students may complete the various assignments within the scheduled periods. It is essential that the individual student formulate his own schedule to conform with the group assignments. To make effective use of the laboratory period the student must be familiar with the analytical operations to be performed. The only way such familiarity can be attained is by an appropriate amount of homework before coming to the laboratory. The procedures for an assigned period should be studied carefully, and an outline may be made of the successive operations to be encountered. Laboratory work should be confined, as much as possible, to manipulations and operations. Use outside time for calculations and the filling in of routine forms in the notebook.

The student might consider a quantitative analysis as being divided into three steps: (1) the attainment of a summarized knowledge of the analysis; (2) the physical accomplishment of the experiment with attendant and pertinent observations; (3) the calculations of the results from the observations. Only the second step should utilize laboratory time.

1·2 Economy of Time. Within the laboratory hours the student may learn to accelerate his laboratory production by attention to various analytical techniques which are described elsewhere. These techniques are mastered only through practice, and are not acquired "overnight". It may not be as easy to perform techniques properly the first time, but it should be remembered that one of the principal objectives of the course is to attain good laboratory skills.

One technique that the student should learn from the beginning is the efficient utilization of laboratory time. Part of this is proper organization of operations, and part of it may be sound judgment. A trained analyst learns to do many things at the same time. For example, certain evaporations, filtrations, and titrations may be performed simultaneously. The average student will probably not become a laboratory analyst, but he should recognize the advantage of doing many operations in the minimum amount of time.

It is common sense for a student to foresee each step in analytical manipulations, and to plan these steps so that no period of waiting occurs between them. If, for some reason, such a period should occur, the resourceful student will be prepared to begin the next analysis in the assigned schedule. For example, practically all samples for analysis must be dried beforehand, and before one analysis is complete, the student should have a dried sample ready for the next analysis.

1·3 Desk Equipment. In Table A·3, in the Appendix, will be found a list of the apparatus issued to each student. However, the list may be modified by the instructor to fit the particular needs of the course. Certain general directions concerning the equipment have wide acceptance. Some of these are as follows:

1. Copy desk number and lock combination in your laboratory manual, and also on a piece of paper to be carried in your billfold.

2. Check desk equipment against the apparatus list; any items missing should be obtained from the main stockroom. Glassware which is cracked, chipped, or badly etched should also be replaced from the storeroom. It is usually necessary to get the instructor's approval for such replacement to avoid extra charge against laboratory deposit.

3. All equipment will be checked by the instructor at the end of the term, and any defective equipment will be charged to the student.

4. It is usually customary for the student to make a breakage deposit to take care of wear and tear on equipment. Part of this deposit may be returned.

5. The equipment should be arranged in the desk to provide maximum availability of the most widely used items, and to insure a minimum loss through breakage of fragile items. If the desk has not been in constant use, it may be necessary to remove all equipment before rearrangement, and to remove any accumulation of dust.

6. Clean the desiccator, and add fresh anhydrous calcium chloride, if necessary. Replacement is indicated when there is evidence of caking. The ground-glass rim of the desiccator should be lightly greased with petroleum jelly to maintain an air-tight seal. Additional instructions concerning the desiccator are to be found in Sec. 5·7.

1·4 Apparatus to be Constructed. In addition to the standard items of equipment listed in Table A·3, it will be necessary for the student to construct a few pieces of apparatus which have special uses in some of the laboratory procedures.

Wash Bottle. The wash bottle is a familiar object in any analytical laboratory. There are many types, but the one produced from a flat-bottomed flask (500 or 1000 ml Florence flask) is typical. The simplest form of this piece of equipment is indicated in Figure 1·1. The fittings are usually made from three pieces of 6 mm glass tubing, cut to the approximate lengths desired. The bends, indicated in the diagram, should be made in the same plane and without kinks. Use a wing tip on the burner so that the tubing can be heated over a wide distance. The tip should have an opening about the same size as found on either a standard burette or ordinary pipette, which is approximately 1 mm in diameter. The tip is connected to the main delivery tube by means of a short piece of rubber tubing of the size to fit snugly. The ends of the pieces of glass tubing should be fire polished before assembling the wash bottle. The instructor may be consulted for additional direction in the techniques of glass working.

Safety Bottle. Ordinary suction filtrations are accomplished by means of a water aspirator connected to a suction flask. Inasmuch as there are usually wide variations in water pressure, such changes may cause water to back up into the flask from the water pump and contaminate the filtrate. A safety bottle inserted between the suction flask and the aspirator will act as a safety valve to prevent such contamination. The safety bottle is constructed by inserting two pieces of glass tubing, bent as indicated in Figure 1·1, into a two-hole rubber stopper which fits an ordinary wide-mouth 250 ml bottle.

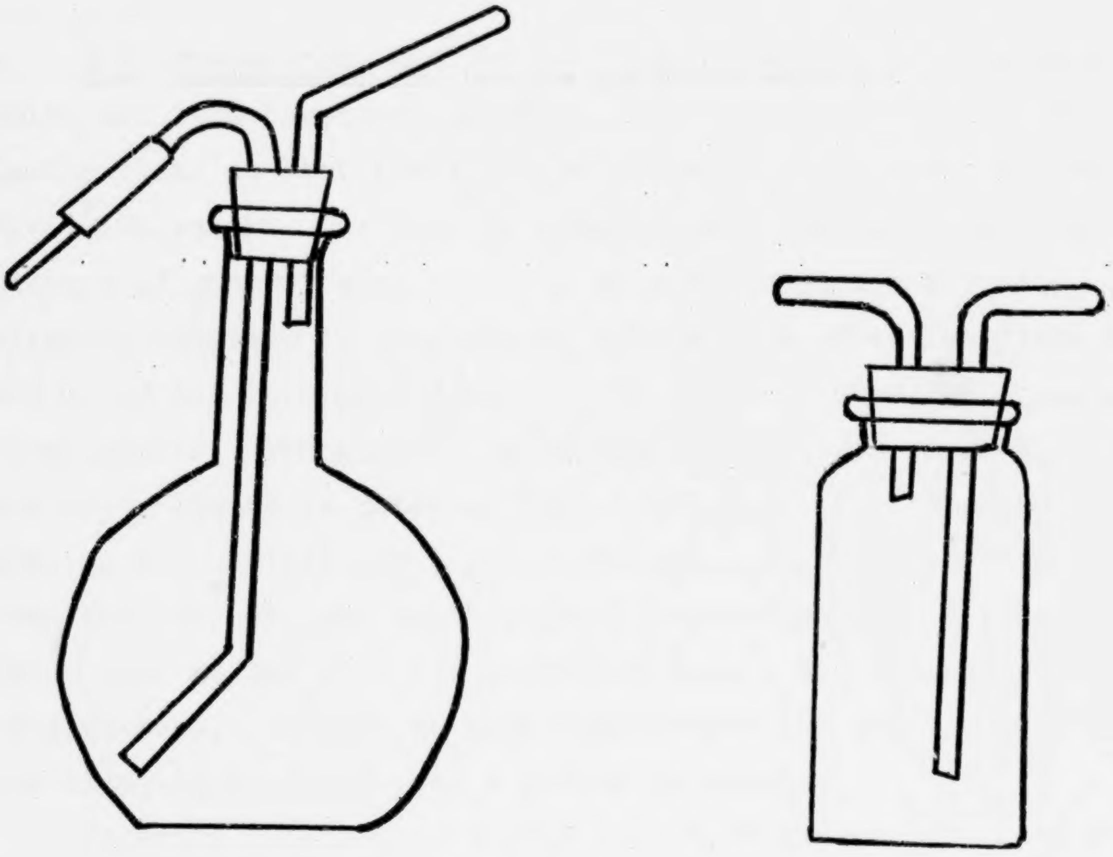

Figure 1·1 Wash Bottle and Safety Bottle.

Stirring Rods. Cut six stirring rods, 5 mm in diameter, each to a length of approximately 150 mm. Fire polish both ends of each rod to prevent scratching of beakers and test tubes. If rods are already present, this construction may be omitted.

CLEANLINESS AND SAFETY

1·5 Preparation and Use of Cleaning Solution. Volumetric glassware, which includes burettes, pipettes, and volumetric flasks, must be sufficiently clean so that their inside surfaces are wetted uniformly with distilled water. One type of reagent used for cleaning purposes is a mixture of concentrated sulfuric acid and sodium dichromate. This cleaning solution is prepared by adding 20 g of sodium dichromate to 400 ml of hot (not more than 100° C), concentrated H_2SO_4 contained in a large beaker. The mixture is stirred and allowed to cool. After cooling, the clear liquid is decanted into a 500 ml glass-stoppered bottle, leaving any undissolved crystals behind. Cleaning solution may be used over and over as long as it retains its red color. A green color indicates that it has lost its oxidizing power, and such a solution should be discarded. If kept at room temperature the solution usually retains its cleaning property over a period of months.

Cleaning solution is highly corrosive and must be used with extreme care. It will destroy clothing, and will produce severe burns on the skin. Any amount, even a drop, spilled on any surface should be neutralized with sodium bicarbonate, and then washed completely with water. When spilled on the skin, it should be removed with running water as quickly as possible.

Hot cleaning solution cleans within ten minutes, but is more dangerous to handle and may cause errors in the volume of calibrated glassware. Cold cleaning solution is equally effective, but slower in action, usually requiring an overnight period of contact.

1·6 Cleaning Glassware. Most glassware is best cleaned with a commercial detergent, applied with a brush, and then removed with several rinsings of water. Usually the detergent is supplied by the instructor or from the stockroom. Use tap water for all washing and rinsing purposes; under no conditions is distilled water to be used except in a small quantity for a final rinse.

The insides of volumetric glassware (burettes, pipettes, and volumetric flasks) should be sufficiently clean so that an even film remains after they are filled and drained with distilled water. A number of recipes for satisfactory cleaning solutions are to be found in the various chemistry handbooks. One that is widely used, although hazardous and corrosive in nature, is the $H_2SO_4 \cdot Na_2Cr_2O_7$ mixture described in Sec. 1·5.

A burette may be cleaned rapidly by drawing warm cleaning solution from a beaker through the action of a water aspirator into the inverted tube of the burette. It is customary to insert a safety bottle in the suction line to prevent the cleaning solution from being drawn into the water pump. The set-up is illustrated in Figure 1·2. Pipettes may be cleaned using a similar procedure. Volumetric flasks are more conveniently cleaned by allowing cold cleaning solution to stand in the flasks overnight. The cleaned volumetric equipment should be rinsed thoroughly with distilled water. If any drops of water adhere to the walls, the item must be recleaned.

Clean burettes should be filled with distilled water and stored in an upright position. If it is necessary to store them in a horizontal position they should be well corked. The new types of burettes with Teflon stopcocks do not leak, and even those with glass stopcocks do not leak when used with a suitable spring clip. Burettes thus stored will stay clean indefinitely.

1·7 Disposal of Waste Products. Waste solids such as match stems, used filter paper, used corks, broken glassware, and old towels must be discarded into stone crocks which are distributed in convenient places in the laboratory. Under no conditions are solids to be allowed in the troughs or drains. A student, thoughtless in this respect, may be the cause of extensive damage to the laboratory plumbing.

Waste liquids are to be discarded directly in the main sink, not in the laboratory trough, and flushed with large quantities of tap water. The disposal of corrosive acids and alkalies must be accomplished in

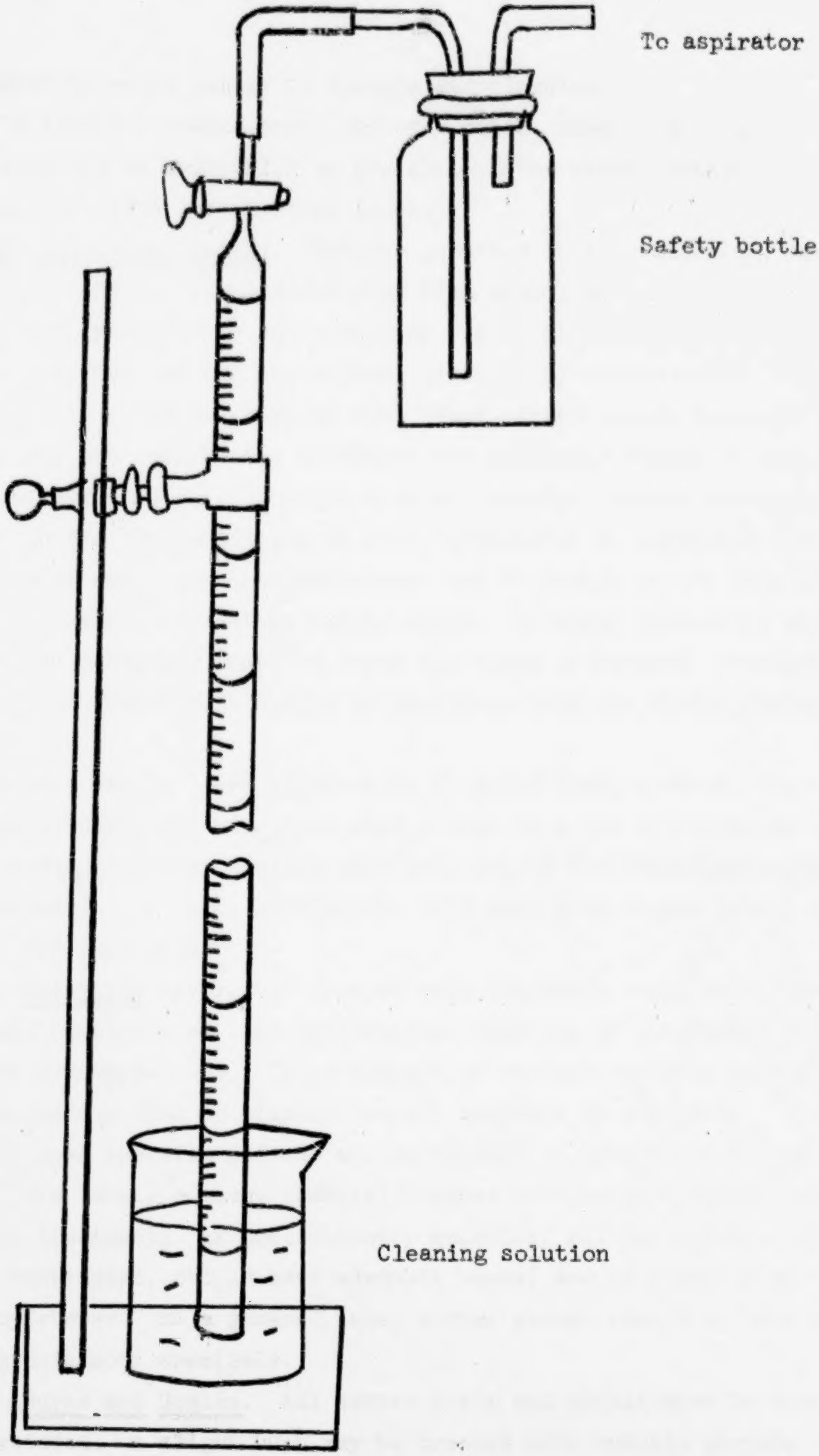
To aspirator
Safety bottle
Cleaning solution

Figure 1·2 Cleaning a Burette.

this manner to avoid damage to troughs and plumbing.

If a liquid contains particles of a solid, decant the liquid into the sink, retaining as much solid as possible in the glass container. Dump any remaining solid into a stone crock.

1·8 Laboratory Safety. Serious injuries in the laboratory are infrequent. Students have learned from high school and general chemistry that laboratory equipment and chemicals are to be respected and, consequently, they use certain precautions dictated by common sense. On the other hand, it sometimes happens that "familiarity breeds comtempt", and students may not realize the hazardous and poisonous nature of certain common chemicals such as hydrogen sulfide, mercury, carbon tetrachloride, etc. It is the responsibility of every instructor to emphasize the importance of safety in the laboratory, and it should be the duty of every student to observe laboratory safety rules. In every laboratory there should be an emergency chart to cover all types of possible accidents. One excellent chart of this type is available from the Fisher Scientific Company.

The best way to treat injuries is to avoid them; however, this is not entirely possible, and there will always be a few accidents in all laboratories. Injuries usually fall into one of the following categories: (1) poisoning, (2) burns and scalds, (3) cuts from broken glass, and rarely, (4) explosions.

Poisoning may result from so many chemicals -- in fact, from nearly all chemicals -- that the cautious handling of laboratory reagents cannot be overemphasized. The treatment of various specific poisons varies so widely that no simple, overall antidote is available. Treatments for some specific poisons are designated on Laboratory Emergency Charts. The labels on many chemical reagent bottles give directions for emergency treatment. As precautionary measures, all laboratories should be well ventilated, should have adequate hoods, and if possible an emergency shower. As a general rule, rubber gloves should be worn while handling poisonous chemicals.

Burns and Scalds. All severe burns and scalds must be treated by a physician. A slight burn may be treated with butesin picrate ointment or sterile petroleum jelly. Do not use ointments on severe burns, but leave any treatment to a physician. Minor burns arising from spilled acids and alkalies should be washed thoroughly with water as quickly as possible, and then treated with neutralizing agents recommended by the instructor, or by the instructions of emergency chart. Burns in the eyes should be washed with large quantities of water. If the burn is due to acid, wash with five per cent solution of sodium bicarbonate; if due to an alkali, wash with a saturated solution of boric acid. Eye burns should always be sent to a physician after the preliminary emergency treatment indicated above.

Cuts. Severe cuts are rare, but if they should occur, consult the emergency chart as to the application of a tourniquet until a physician arrives. Minor cuts may be treated with tincture of merthiolate, and then covered with sterile gauze.

1·9 Terminating the Laboratory Period. The laboratory desk and its contents should be kept orderly, clean and neat at all times. Satisfactory laboratory techniques will permit the student to spend a minimum amount of time in terminating a laboratory period. The instructor will expect each student to store all equipment in his desk at the end of each laboratory period, and each desk should bear inspection if necessary. The working area should be sponged lightly with a small amount of cleaning powder, and then thoroughly rinsed with water to remove excess powder and dirt, before leaving the laboratory. In return the student should expect to find the top of his desk completely clean at the beginning of a work period.

REAGENTS

1·10 Care and Use of Reagents. A list of reagents used in the experiments is given in tables in the Appendix. Recipes for making special solutions are given within the same tables. As a general rule, only reagents of highest purity are purchased for use in the quantitative analysis course. Inasmuch as many of these reagents are expensive, it is expected that they be used sparingly and with reasonable care.

The following precautions should be generally observed in the use of reagents in a quantitative analysis laboratory:

(1) Reagents in general. Reagents must not be contaminated by inserting dirty instruments into reagent containers. Reagent bottles should be kept tightly stoppered when not in use.

(2) Liquid Reagents. A solution should be poured from its bottle, in the volume estimated as necessary, into a clean, dry beaker or graduate. Never insert a pipette into a reagent bottle. In order to avoid waste, remove only what you will probably need; but do not return any unused portion to the bottle. Stoppers of reagent bottles should be held in the hand while pouring and then replaced immediately.

(3) Solid Chemicals, used in preparing solutions, are to be weighed on a general laboratory balance (not the analytical balance) unless otherwise directed. Remove directly from the bottle--by slightly tilting--to a piece of glazed paper on the balance pan. It is permissible to use a clean spatula to loosen the solid chemical within its container. Never place a chemical directly on the balance pan. If a small excess is poured out, discard into a stone waste jar. If any large quantity of a solid is spilled, consult the instructor at once. Keep the top of the general balance, and the desk top about it, free from chemicals and waste paper. Spillages must be cleaned up at once using your sponge or towel.

1·11 Distilled or Deionized Water. Distilled (or deionized) water is the most important reagent in the analytical chemistry laboratory. Even distilled water may contain impurities. Soluble or insoluble impurities may occasionally be carried over in the distillation process, and gases from the atmosphere will contaminate distilled water upon standing. The procedures of elementary quantitative analysis rarely require ultra-pure water, and usually ordinary distilled or deionized water is satisfactory. Dissolved gases from the air may be removed by boiling and proper storage when necessary.

Tap water is always contaminated with impurities which may affect chemical analyses, but tap water is usually of sufficient purity for washing purposes. Distilled water is so expensive and difficult to produce and store, that it should never be used for washing purposes except under unusual conditions specified by the laboratory procedures or by the instructor. In other words, the student should appreciate the presence of sufficient distilled water, and should not abuse this convenience by wasting the water.

Distilled water is used for all solutions. It may be used for rinsing purposes *from a wash bottle*. *Under no conditions is washing or rinsing permitted at the distilled water tap*.

USE OF THE ANALYTICAL BALANCE

Most courses in quantitative analysis make use of one-pan electric balances for analytical weighings. Such balances are made by a number of manufacturers, and the majority are excellent instruments. The balance described in these procedures is the Mettler H15; however, the use of any other analytical one-pan balance involves essentially the same manipulations.

1·12 Fundamental Rules for Maintaining Accuracy and Reproducibility. Each balance is assigned to a group of individual students; once having been assigned to a particular balance, a student should use it exclusively. Although modern analytical balances are quite accurate, there are always slight differences in the weights which are built into the balance. When using the same balance for a given analysis, errors caused by slight differences in weights usually cancel out. On the other hand, such a cancellation of errors may not occur if more than one balance is used in a single analysis.

The following rules should be observed with the use of an electric one-pan balance:

(1) The balance should be placed where it will be free from vibration.

(2) The balance should be leveled by means of the built-in spirit level before attempting a weighing operation.

(3) Objects to be weighed should be placed on the balance pan only when the balance is arrested. The same rule applies for removing objects. The Mettler balance has a knob on the left side of the balance case (Fig.

1·3), which may be turned to three different positions. When the knob pointer is vertical (points upward) the balance is arrested; if the knob is moved forward (toward the operator) the balance is semi-released; and when the knob is moved backward (away from the operator) the balance is fully released.

(4) *Turn the weight-setting knobs only when the balance is semi-released*. As has been stated before, the semi-released condition is attained when the knob on the left side of the balance is turned toward the operator.

(5) *The side windows of the balance must be shut before the balance is fully released*. Air motion through the balance can cause the pan to fluctuate sufficiently to give inaccurate weighings.

(6) *If the balance is out of adjustment, consult your instructor*.

1·13 Procedures for Weighing. The following rules should be observed in a weighing operation:

(1) *The balance pan must be clean*. If necessary open the window and brush the pan with a camel's hair brush.

(2) *Set all weight knobs (located on front of the balance--Fig. 1·3) on zero*.

(3) *The optical scale and vernier scale should coincide on the zero positions*. Release the balance completely, by moving the knob on the left side of the balance backward. When the optical scale comes to rest, bring the zero of this scale (using the adjusting knob on the right side of the balance case--Fig. 1·3) to a position so it will coincide with the zero line on the vernier scale. These two scales are illuminated from within the balance case: the movable one on the left is designated as the optical scale, and the smaller fixed-position one, on the right, is described as the vernier scale.

(4) *After the zero point has been checked and adjusted, return the balance to the arrested position*.

(5) *Place objects on pan when balance is in the arrested position*. All objects to be weighed must be dry and at room temperature. Use tweezers or piece of folded paper to handle objects to be weighed. (Moisture from the fingers will affect weighings.) Close the balance window immediately after object is placed on the pan.

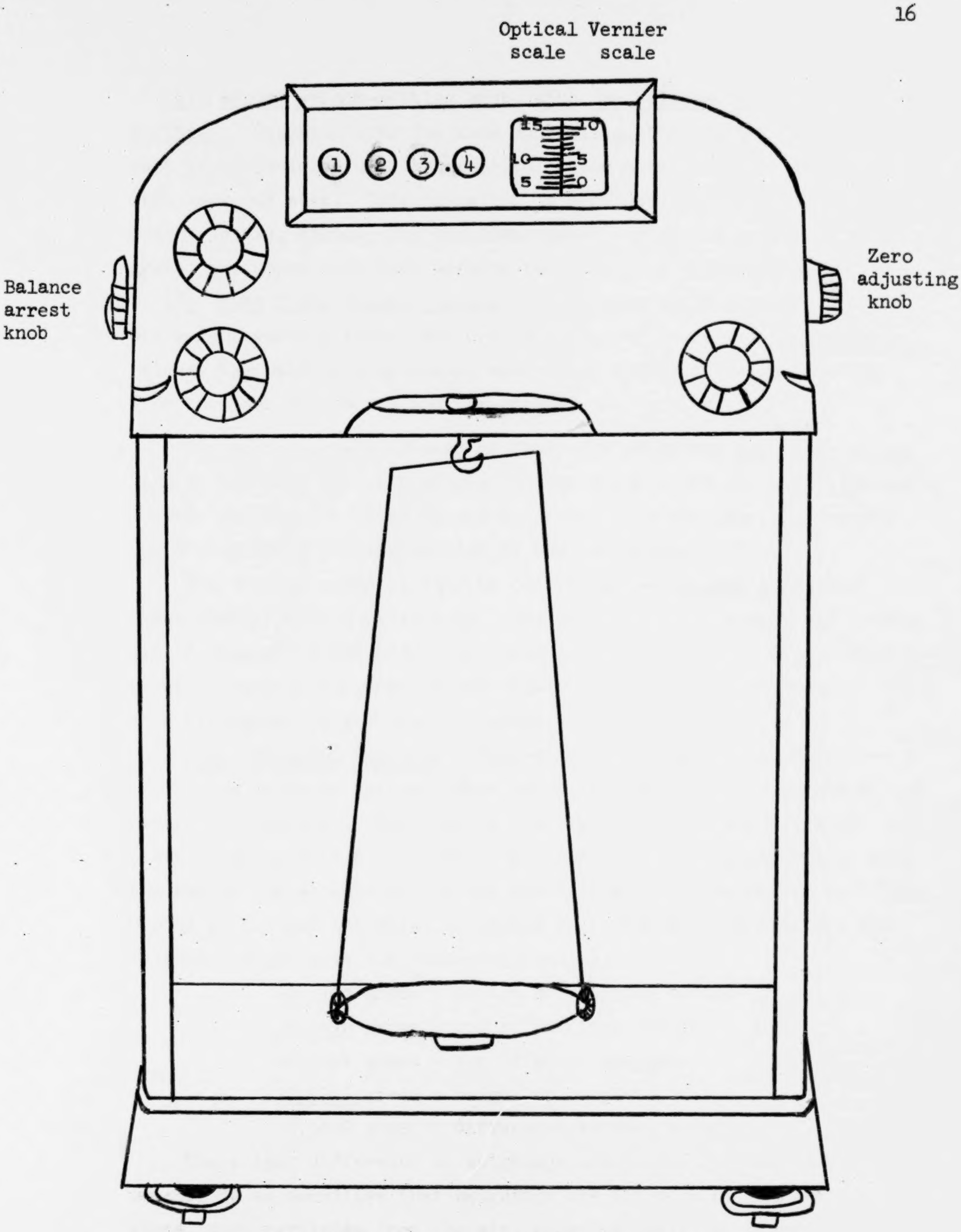
Optical scale
Vernier scale
① ② ③.④
15
10
5
10
5
0
Balance arrest knob
Zero adjusting knob

Figure 1·3 An electric one-pan balance

(6) Adjust weight-setting knobs with the balance in the semi-released position. Starting with the knob controlling the heaviest weights turn each knob clockwise until the optical scale moves upward. Then turn the knob back one step. This operation is performed for each of the three weight-setting knobs. The two lower knobs adjust the number of whole grams; the upper left knob adjusts the number of tenth-grams.

(7) Make final weight reading with balance fully released. After the weight-setting knobs have been adjusted as described in Step (6), release the balance completely, and record the final weight reading from the knob indicators and the optical and vernier scales.

The optical scale is read by observing where the zero line on the vernier contacts the optical scale. For example, if the zero line falls between calibration lines 50 and 51 on the optical scale, the optical scale reading is 50--the smaller of the two values.

The vernier scale is read by observing the vernier line which coincides exactly with a calibration line on the optical scale. If vernier line 3 happens to coincide, the vernier reading is taken as 3. With the vernier reading, the mass of the object is recorded to the nearest tenth of a milligram; e.g., 129.7503 grams.

1.14 Weighing Exercise. Determine the weight of the bottom of a clean, dry weighing bottle. Next weigh the top of the same bottle, and record both weights. Now combine the top and bottom and weigh the complete weighing bottle. Compare the weight of the complete bottle with the sum of the weights of the top and bottom. If they differ more than 0.0003 g (0.3 mg) the weighing should be repeated. For example, the weighings might give the following results:

14.6728 grams = bottom of weighing bottle
8.2416 grams = top of weighing bottle
22.9144 grams = sum of above weights
22.9146 grams = weight of complete bottle
0.0002 gram = difference between weighings

The slight difference in weighings are generally unavoidable. The balance is so sensitive that weighings are affected by temperature variations, dust particles from the air, relative humidity, adsorption of traces of moisture by the weighed object, and uncertainties in reading the vernier scale. However, differences greater than 0.3 mg imply misreading of the scales or other experimental error.

THE QUANTITATIVE LABORATORY NOTEBOOK

1·15 Suggestions for Keeping Notebook. Different teachers may have slightly different preferences as to the keeping of laboratory records. However, through many years of experience, the method of keeping a laboratory notebook has evolved along certain general lines, so that there is not much difference between the form used by a beginning student in quantitative analysis and the form used by a research chemist.

Laboratory records are usually kept in a stiff-backed, bound notebook with pages numbered, measuring $7\frac{1}{2}$ x $9\frac{1}{2}$ inches. The notebook is expected to be a complete, accurate, and original record of all experimental work and the related calculations. The following suggestions are offered, which may be modified to the needs of the student and the instructor:

(a) *Never* tear a page from the notebook [see (g) below].

(b) Use a *medium, black* pencil instead of a pen.

(c) Reserve pages 1-4 for an *index* to be compiled as work progresses.

(d) Commence the record of each experiment at the top of a *right-hand* page, headed as follows:

Experiment No..... .... (Object of experiment) .... (Date)

(e) Enter on this page, *at the time they are made, all observations* (weighings, burette readings, etc.) following the model forms given in this section. Continue with the necessary equations, calculations, and summary of results. Do not crowd your work; take all the space needed for clarity; if one page is not sufficient, pass to the next right-hand page.

(f) Use the *left-hand* pages for making incidental calculations and for any purpose for which scratch paper is ordinarily used. The use of loose pieces of paper for any kind of laboratory records or calculations is expressly forbidden.

(g) Correct minor errors by neat erasures. Such errors are those which are recognized at the time they are recorded. When errors are discovered which necessitate extensive recalculations, do not try to erase but strike out the original work with a single diagonal line and refer, by number, to the page on which the new work is found.

(h) It is expected that all calculations will be based upon actual observations, and that observations or figures will not be altered with the object of forcing a better agreement of results.

1·16 Calculations. For many years it was customary for calculations in quantitative chemistry to be performed through the aid of five-place logarithm tables. Such computations were necessarily laborious and time-consuming. Within recent years electric automatic calculators have become available in many laboratories for student use. The operation and care of such calculators will be explained by the instructor, but the student should be forewarned that calculators may be easily jammed necessitating expensive repairs. Two cardinal rules should be stressed:

(1) Do not punch a button on a calculator while it is in operation.

(2) Do not punch two control buttons at the same time.

Round off all results to four significant figures. The retention of a fifth figure pretends to a degree of accuracy that is not warranted by the equipment and methods of the laboratory procedures.

The student may make his calculations in the laboratory if time permits; see Sec. 1·1 concerning planning and scheduling of time. Unless calculations are performed immediately after a series of simple titrations a student may not know whether he has attained the required precision, as, for example, in the determination of the ratio between a base solution and an acid solution. Thus, time may be gained by doing simple calculations at the time the observations are made. On the other hand, if the calculations are sufficiently complex to be time-consuming, they should be delayed until the laboratory work is completed.

Specimen forms illustrating hypothetical notebook records are given in Table 1·1 and Table 1·2.

Table 1·1 Specimen of a Volumetric Determination

Exp. 2·11 Percentage Composition of Impure Potassium Acid Phthalate Date 10/5/65

Samples	A	B	C
Wt. of weighing bottle + sample	31.6242 g	30.5177 g	29.6569 g
Wt. of weighing bottle - sample	30.5177 g	29.6569 g	28.6662 g
Wt. of sample	1.1065 g	0.8608 g	0.9907 g
Burette reading (initial)	0.30 ml	0.14 ml	0.20 ml
Burette reading (final)	36.30 ml	28.17 ml	32.44 ml
Ml of NaOH added	36.00 ml	28.03 ml	32.24 ml

General formula:

$$\frac{\text{ml NaOH} \times \text{N NaOH} \times \text{meq wt KHP} \times 100}{\text{wt. of sample}} = \text{per cent KHP}$$

(A) $\frac{36.00 \times 0.1020 \times 0.2042 \times 100}{1.1065} = 67.77$ per cent KHP

(B) $\frac{28.03 \times 0.1020 \times 0.2042 \times 100}{0.8608} = 67.82$ per cent KHP

(C) $\frac{32.24 \times 0.1020 \times 0.2042 \times 100}{0.9907} = 67.78$ per cent KHP

		Deviation	Deviation parts/thousand
Sample A	67.77	0.02	0.3
Sample B	67.82	0.03	0.4
Sample C	67.78	0.01	0.1
	3)203.37	3)0.06	3)0.8
	67.79	0.02	0.3

Per cent Potassium acid phthalate = 67.79 Deviation = 0.3 parts/M

Table 1·2 Specimen of a Gravimetric Determination

Exp. 5·10 Gravimetric Determination of Chloride in a Soluble Salt Mixture Date 1/6/66

	Sample A	Sample B
Wt. of weighing bottle + sample	26.0297 g	25.5976 g
Wt. of weighing bottle - sample	25.5976 g	25.0940 g
Wt. of sample	0.4321 g	0.5036 g
Wt. of empty Gooch crucible	A	B
After 1st heating	16.7423 g	16.8926 g
After 2nd heating	16.7421 g	16.8923 g
	A	B
Wt. of Gooch crucible + AgCl	17.2826 g	17.5205 g
Wt. of Gooch crucible	16.7421 g	16.8923 g
Weight of AgCl	0.5405 g	0.6282 g

General formula: $\frac{\text{Cl}}{\text{AgCl}} \times \frac{\text{wt. AgCl}}{\text{wt. of sample}} \times 100 = \text{per cent Cl}$

Sample A

$$\frac{35.45}{143.3} \times \frac{0.5405}{0.4321} \times 100 = 30.94$$

Sample B

$$\frac{35.45}{143.3} \times \frac{0.6282}{0.5036} \times 100 = 30.85$$

		Deviation	Deviation parts/thousand
Sample A	30.94	0.04	1
Sample B	30.85	0.05	2
	$2\overline{)61.79}$	$2\overline{)0.09}$	$2\overline{)3}$
Average	30.90	0.045	2

Per cent Chlorine = 30.90 Deviation = 2 parts per thousand

1·17 Number of Determinations. The actual number of samples that a student should carry through a given analysis may depend upon a variety of factors, which will be discussed in the classroom. These factors are usually treated under a topic stated as, or related to, The Evaluation of Analytical Data. However, it frequently becomes necessary for a student to make a rough evaluation of his laboratory work before the subject is discussed elsewhere.

Two of the factors which may influence the number of determinations are those of precision and accuracy. These two terms have quite different meanings. The precision of a group of results refers to the agreement among the various numerical results obtained by the experiments. In other words, precision indicates the degree of reproducibility. The term accuracy refers to the agreement between the numerical result and a hypothetical true value. Absolute true values can never be attained but they may be approached. In actual practice, true values are defined within certain limits, which are dependent upon the accuracy of the instruments and the skill of the operators.

It is sometimes frustrating to a student when he obtains results which are close together (precise), but which are found to be far from the true value (inaccurate). The accuracy of student determinations is usually evaluated by the instructor, on the basis of results obtained from multiple analyses of professional analysts.

The precision (and also accuracy) of analytical results is customarily expressed as an average deviation in parts per thousand. The computation of this expression involves four essential steps, which may be described as follows:

(1) Calculate the arithmetical mean of the results.
(2) Compute the deviation of each result from the average, ignoring its algebraic sign.
(3) Obtain the average deviation of all observations.
(4) Multiply the average deviation by 1000 and divide by the average result to get average deviation in parts per thousand.

These steps are illustrated by using the following hypothetical observations:

	Observations		Deviations from the average
	35.46		0.09
	35.62		0.07
	35.57		0.02
	3)106.65		3)0.18
Average observation	35.55	Average deviation	0.06

$$\frac{0.06 \times 1000}{35.55} = 2 \text{ parts per thousand (approximately)}$$

Duplicate determinations must be made, otherwise a student has no criterion for calculating the precision of his work. Inasmuch as a beginning student frequently ruins one sample of a determination, it is usually desirable to make triplicate determinations. The student will soon realize that the three determinations can be performed simultaneously almost as quickly as a single determination.

The statistics of the variation of accuracy and precision has been studied for over 300 years, and has become progressively more complex. Such studies, including the rejection of results, will be discussed in the classroom. However, it can be said that an average result is more apt to be accurate when a large number of determinations are involved. But this accuracy is only increased, roughly, in proportion to the *square root* of the number of determinations; thus, many determinations are not significantly more accurate than a few.

Agreement of duplicate or triplicate results, in carefully tested procedures, is a good indication that the error in the analysis is small, but does not constitute proof of such. In other words, close agreement indicates excellent precision, but not necessarily close accuracy. A student should strive to attain a precision, *i.e.*, agreement of results, of two parts per thousand. Most quantitative laboratories have equipment, for student use, which permits the attainment of this range of precision. Three parts in one thousand is usually satisfactory, but when the precision drops below five parts in one thousand, the accuracy is very likely to be poor. A precision as low as ten parts per thousand is not acceptable.

1·18 Reports and Grades. No experiment is complete until the results have been calculated, in the notebook, reported on a separate sheet of paper, and accepted by the instructor. The authors have found it to be expedient to require that all reports should follow the forms given in Table 1·1 and Table 1·2, and be submitted on sheets of notebook paper measuring 8½ x 11 inches. Such reports are graded and retained by the instructor so that they may be available for future use. Occasionally a student makes a gross error in arithmetic in calculating a determination, which may not be discovered until quite some time after the report is made. It is advantageous to the instructor to have a copy, as given on the report, of all pertinent observations, as well as general formula for the calculations. Since the purpose of the laboratory work is to illustrate methods and techniques of analysis, the authors believe that a student should not be penalized to a failing grade because of an arithmetical error; consequently, a complete report will be a protection to both the student and the instructor.

Laboratory work is graded: (a) on its accuracy, as judged by the agreement of the duplicates (or triplicates) with the values known to the instructor; and (b) on the prompt submission of a neat, orderly report. Work definitely deficient in either respect will not receive a satisfactory grade.

Different teachers will have varying methods of grading laboratory work in quantitative analysis. In Table 1·3 the authors present one method of grading which may be of assistance to beginning teachers. No pretense is made as to the accuracy of this method of grading.

Table 1·3 A Grading System for Determinations in Quantitative Analysis

(Deviations are from values known only by the instructor.)

Deviations in parts per thousand	Grade
0.0 - 5.0	A
5.0 - 10.0	B
10.0 - 15.0	C
20.0 - 25.0	D
25.0 - 30.0	E
Below 30.0	F

Regulations Regarding Reports

All reports must contain at least duplicate results which should check within ten parts per thousand of each other.

Reports should be submitted on notebook paper measuring 8½ x 11 inches. They must contain all pertinent weighings, titrations, and calculations as indicated in the examples given in Table 1·1 and Table 1·2. Arithmetical errors occurring upon a report sheet may be corrected without penalty. Errors not indicated on the report sheet cannot be removed, and such errors will enter into the grading computations.

Chapter 2

NEUTRALIZATION METHODS

PREPARATION OF ACID AND BASE SOLUTIONS IN BULK

2·1 Preliminary Comments. The reaction of hydroxide and hydronium ions with each other, or with other acids or bases, forms the foundation for neutralization methods. For a quantitative determination the reaction should produce a rapid change in pH near the equivalence point. This change may be observed with either a pH meter or by color changes in suitable acid-base indicators.

The best solutions for acid-base titrations contain strong acids or bases. Such reagents must be fairly soluble and relatively inexpensive. The resulting solutions should be stable, and should not produce side reactions when used in acid-base determinations. Only a few acids and bases meet these criteria. The most satisfactory acids are hydrochloric and potassium hydroxide. However, strong bases have a tendency to react with glass containers, and absorb CO_2 when exposed to the atmosphere; consequently, certain precautionary measures are necessary in the preparation and use of base solutions.

2·2 Preparation of Approximately 0.1 N HCl Solution. Measure as accurately as possible with a small graduated cylinder, 17.5 ml of reagent-grade concentrated HCl (specific gravity 1.185 - 1.192), and pour this amount into a one-liter volumetric flask. Rinse the graduate with two portions of distilled (or deionized) water, and add rinsings also to the flask. Fill the volumetric flask approximately to mark with distilled water, and then transfer the solution to a clean five-pint bottle. (Non-returnable acid bottles are excellent for this purpose.) Fill the flask once more to mark with distilled water, and pour the additional liter of water into the bottle. This gives a total volume of two liters approximately measured. Stopper the bottle tightly, and then thoroughly mix the contents by inverting repeatedly and shaking for at least ten minutes. Label the bottle neatly as follows:

0.1 N HCl

Your name   Date

Store the bottle of 0.1 N HCl inside the desk cabinet until needed.

Concentrated HCl is very close to 12 normal; hence, when 17.5 ml is diluted to a total volume of 2 liters (2000 ml) the resulting solution will be approximately 0.1 N:

$$ml_1 \times N_1 = ml_2 \times N_2$$

or

$$17.5\text{ ml} \times 12\,\frac{\text{meq}}{\text{ml}} = 2000\text{ ml} \times N_2$$

$$N_2 = 0.105\,\frac{\text{meq}}{\text{ml}} \text{ or } \frac{\text{eq.}}{\text{liter}}$$

Normality, molarity, and formality may be used interchangeably as far as HCl and NaOH are concerned; the distinction between these three terms will be considered in the classroom.

2·3 Preparation of Approximately 0.1 N NaOH Solution. Using a one-liter volumetric flask, measure two liters of distilled (or deionized) water into clean beakers. Heat the water to boiling, cool until warm, and then transfer to a two-liter borosilicate glass bottle. Stopper tightly with a solid rubber stopper.

By means of a small graduated cylinder, measure 10.5 ml of clear, fifty per cent, reagent-grade sodium hydroxide solution*, and add the measured quantity to the two liters of freshly boiled water. Mix the resulting solution thoroughly by inverting repeatedly, and shaking, for at least ten minutes. Label the bottle 0.1 N NaOH, with your name and date, as indicated in the preceding section and store in the desk until needed. It is essential that the solution should be kept well-stoppered at all times to prevent absorption of carbon dioxide from the air.

Fifty per cent sodium hydroxide is approximately 19 N and is fairly free of carbonate ions, since sodium carbonate is insoluble in this high concentration of hydroxide ions. When 10.5 ml is diluted to an approximate volume of two liters the resulting solution will be approximately 0.1 N.

*Warning. Use care to prevent the concentrated NaOH from coming into contact with the skin, since this substance can produce severe burns. See Sec. 1·8 for treatment of such burns.

COMPARISON OF STRENGTH OF ACID AND BASE SOLUTIONS BY TITRATIONS

2·4 Preliminary Comments on Titrations. Volumetric analysis involves the addition of an equivalent amount of a known material to a measured amount of unknown substance. When a burette is used to measure out the added amount, the procedure is known as a titration. An end point occurs when there is a definite recognizable change in the solution being titrated. The end point may be a change in the color of a suitable visual indicator, or it may be some other sharp change in a physical or chemical property of the solution being titrated. The equivalence point in a titration occurs when the number of equivalents of material in the titration flask is just equal to the number of equivalents of titrant added. Some acids, possessing more than one removable proton, may show more than one equivalence point during a titration.

Titrations with visual indicators are stopped exactly at the end point and are designed so that the end point will occur near the equivalence point (e.g., procedures in Sec. 2·6 and 2·7). However, where graphical methods of analysis are used (e.g., Sec. 2·8), the equivalence point may be determined more precisely if one continues to take measurements beyond the end point.

When the pH of a solution is plotted versus the ml of titrant added, an S-shaped curve is obtained. The S-shape occurs as a result of the very rapid change in pH in the area of the equivalence point. The equivalence can be detected graphically by determining the point at which the rate of change of pH is greatest. This point is usually midway along that portion of the S-curve which is most nearly parallel to the pH axis. It is difficult to locate the point graphically unless the entire S-curve is plotted.

A number of highly colored organic dyes have the property of changing color when the pH of a solution is varied between certain limits. These dyes are called visual acid-base indicators. For a visual indicator to be satisfactory for a quantitative acid-base determination, it must change color abruptly at a point which coincides closely with the equivalence point. Since most visual indicators require a change of 2 pH units before their color change is distinct enough for satisfactory detection, there must be a sharp change in the pH of the solution in the vicinity of the equivalence point to permit the use of such an indicator. Phenolphthalein is useful for the titration of weak acids by a carbonate-free base; it undergoes a color change from colorless to pink at a pH of approximately 9.5. The most suitable indicator for carbonate titrations is a mixture of two particular dyes: methyl red and bromcresol green. This mixed indicator, when used after boiling to remove carbon dioxide, produces a satisfactory color change from pink to green at a pH of approximately 5.0. The two indicators jointly produce a more distinct and more abrupt color change than either indicator does separately.

2·5 Preparation of Burettes for Titrations. By means of small paper labels, identify each of your two burettes near their tops as HCl and NaOH. It is convenient, and tends to avoid error, to always place the burettes in a given order, *e.g.*, the *acid* always to the left. Rinse the previously cleaned burettes (see Sec. 1·6) at least four times with small portions of the respective solution to be placed in the particular burette; namely, HCl in the left burette, and NaOH in the right burette. Discharge rinsings through the tips of the burettes.

Fill the burettes with their respective solutions to a point considerably above the top graduation mark, and then open the stopcock completely on each burette until all air bubbles have been removed from the tip. The final solution level should be just below the 0.00 ml mark. Do not try to adjust to exactly on the zero mark. Remove drops clinging to the tips of the burettes by touching against the side of the waste-solution beaker. Read the lower level of the miniscus formed by the solution in each burette in such a fashion as to avoid parallax (see Fig. 2·1). Record these readings in an orderly fashion on a right-hand sheet in the laboratory notebook (see Table 2·1). The set-up is now ready for performing a titration.

2·6 Acid-base Ratio with Phenolphthalein as the Indicator. Having recorded the original readings of both burettes, place a clean 500 ml wide-mouth Erlenmeyer flask on the white tile of the burette stand under the acid burette. Run into the flask, down the side to avoid spattering, approximately 30-35 ml of the HCl solution. (It is not necessary to record the burette reading at this stage.) It is correct technique to use the left hand, with fingers curled around the burette, to control the burette cockstop. Use the right hand for rotating the titration flask to produce proper mixing.

Wash down the sides of the flask with distilled water by means of a wash bottle, and then add 2-3 drops of phenolphthalein solution. Since phenolphthalein behaves as a weak acid in the acid-base reaction, more than 2 or 3 drops of the indicator will produce an error in the determination of the ratio. Place the titration flask under the NaOH burette, and run in this solution fairly rapidly, with constant slow rotation to secure proper mixing, until a red color pervades the entire solution. Discharge the color by the cautious addition of HCl. Finally, add NaOH, drop by drop, with constant rotation after each addition until one drop gives the end point. This is a faint pink color, just visible against a white background, but persisting at least 15 seconds. Immediately take and record final readings of both burettes (see Table 2·1). Discard contents of Erlenmeyer flask, and rinse at once with distilled water.

Refill both burettes (rinsing at this time is of course unnecessary), read and record. Make a second acid-base ratio determination as before. Then complete a third in a like manner.

Before proceeding to Sec. 2·7, which involves the use of a mixed indicator, calculate the three ratios just determined and compute the mean deviation (see Table 2·1). Use electric calculator or five-place logarithms for all calculations, and it is usually wise to double check all such computations.

If the mean deviation is less than 4 parts per thousand (a good analyst can secure 1 to 2 parts per thousand or less) take the average of the three as the volume of HCl neutralized by 1.000 ml of NaOH. If this agreement is not obtained, it will be necessary to determine additional ratios until satisfactory results are secured. Erratic results may signify that the HCl and NaOH stock solutions have not been shaken sufficiently to be homogeneous (see Sec. 2·2 and 2·3).

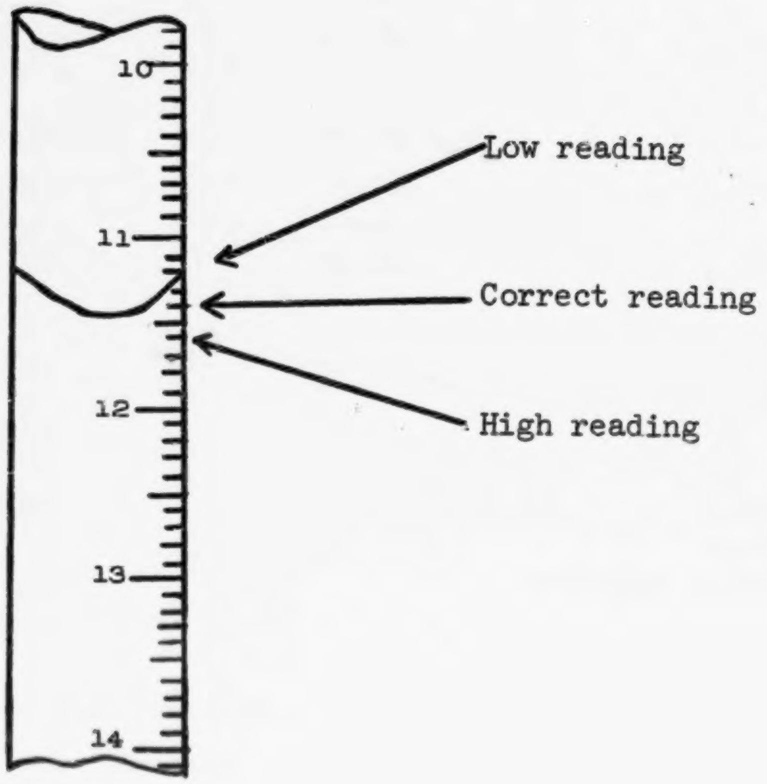
10
11
12
13
14
Low reading
Correct reading
High reading

Fig. 2·1 Correct Method for Reading a Burette to Avoid Parallax.

Table 2·1 Volume-ratio of HCl and NaOH with Phenolphthalein as the Indicator

HCl	NaOH	HCl/NaOH	Deviation
36.46 ml	36.10 ml		
0.36	0.20		
36.10	35.90	1.016	0.002
37.21 ml	36.90 ml		
0.34	0.46		
36.87	36.44	1.012	0.002
38.41 ml	37.80 ml		
0.35	0.21		
38.06	37.59	1.013	0.001
		Average 1.014	Average 0.002

$$\text{Average deviation per thousand} = \frac{0.002 \times 1000}{1.014} = 2/M$$

Therefore, the acid-base ratio is 1.014 ml HCl/ml NaOH with phenolphthalein indicator.

2·7 Acid-base Ratio with Mixture of Methyl Red and Bromcresol Green as the Indicator. Commence the record on a fresh right-hand page of the notebook. Having refilled, read, and recorded the burette readings, run into a clean, wide-mouth Erlenmeyer flask, approximately 35 ml of the NaOH solution, taking care to avoid spattering. Wash down the walls of the flask with distilled water, using wash bottle. Add one drop of methyl orange indicator and titrate with HCl until a definite color change is obtained, and then add one ml of HCl in excess. Do not take a burette reading at this point since more acid is required to complete the titration. The methyl orange indicator is used to make certain that the pH of the solution is definitely in the acid range.

Place the flask on a wire gauze and heat over a free flame until the solution comes to a boil; then continue to boil gently for about one minute. Cool to room temperature, which may be hastened by running cold tap water on the outside of the titration flask. Add 2 or 3 drops of the mixture of methyl red and bromcresol green, and titrate slowly with NaOH solution until a green color is obtained. Now back-titrate with acid to a pink color; then add the base a drop at a time until one drop gives a sharp change to green. It is advisable to approach the end point by the addition of base in each titration. Read both burettes and record the results.

In a like manner, run two more determinations using the mixed indicator solution. Calculate the ratios and deviations (see Table 2·1) and, if necessary, make additional determinations until a satisfactory agreement is obtained. A careful analyst can secure an average deviation of two parts in a thousand, or less.

Theoretically the difference in the ratios obtained with phenolphthalein and the mixed indicator should be about 3 or 4 parts in a thousand. However, in practice the difference in the ratios obtained in Sec. 2·6 and Sec. 2·7 may be five parts in a thousand or more, depending upon the analyst's judgment of the end points. Since the phenolphthalein end point is obtained in a basic solution, and the end point for the mixed indicators occurs in an acid solution, the acid-base ratios for the two different indicators cannot be the same. The reasons for a difference will be considered in the classroom.

2.8 Titration Involving a pH Meter. The purpose of this titration is to demonstrate the use of a pH meter in performing an acid-base titration and to illustrate how the pH of a solution changes as the titration proceeds. Due to the limited number of pH meters available for use by the class, each student will be assigned use of a pH meter for only one particular day. ALL NECESSARY EXPERIMENTAL WORK WITH THE pH METER MUST BE PERFORMED ON THAT ONE DAY.

Principles. A pH meter is, in effect, a high-impedance voltmeter which measures the difference in potential between two electrodes, when they are immersed in a solution. One of the electrodes used is a saturated calomel electrode, with internal parts composed of a mixture of Hg and Hg_2Cl_2 (calomel) in contact with saturated KCl solutions; it is known as a reference electrode, because its potential remains constant, $\mathcal{E}'_{ref}$. The other electrode is a glass electrode, also called a pH indicator electrode; a fragile bulb of specially-prepared glass at its tip causes the electrode's potential to depend upon (i.e., to indicate) the concentration of hydronium ion in the solution. The potential of the indicator electrode varies according to the Nernst equation $\mathcal{E}_{ind} = \mathcal{E}'_{ind} + \frac{2.3\ RT}{n\mathcal{F}}(\log_{10}[H^+])$. Since $pH = -\log_{10}[H^+]$, the pH of the solution is directly related to the potential of the electrode and can be measured on a linear scale. The net difference in potential between the two electrodes is:

$$\mathcal{E}_{ind} - \mathcal{E}_{ref} = \mathcal{E}'_{ind} - \mathcal{E}'_{ref} + \frac{2.3\ RT}{n\mathcal{F}}(\log_{10}[H^+])$$

or,

$$\Delta\mathcal{E} = \Delta\mathcal{E}' - \frac{2.3\ RT}{n\mathcal{F}}(pH).$$

Differences in electrode potential are customarily expressed in "volts" or "millivolts".

Before a pH meter is used for measuring the pH of an unknown, it must be calibrated with a solution of constant known pH, a buffer solution. One dial is used to account for the temperature of the solution; in effect, it adjusts the proportionality factor, $\frac{2.3\ RT}{n\mathcal{F}}$, to the proper value via electrical circuitry. The other dial is used to set the meter needle to read the pH value of the buffer; it subtracts out the value of the constant, $\Delta\mathcal{E}'$, so that the meter reads directly in pH units rather than in volts ($\Delta\mathcal{E}$). Once the pH meter has been calibrated, it may be used to measure the pH of an unknown solution or of a solution during titration.

More details about the theory and working of pH meters can be found in Meites and Thomas, "Advanced Analytical Chemistry", Chapter 4, or in numerous other textbooks of advanced quantitative analysis, analytical chemistry, and instrumental analysis. Operating instructions for the particular pH meters used in the following experiments are given in the Appendix.

Graphical titration requires no visual indicators, since the graph provides needed data; however, the directions of the present experiment call for the addition of indicators so that you can observe the pH ranges over which some indicators change color and judge their applicability in various pH titrations.

The following pH titration is intended merely to be illustrative, so it is not necessary to check for precision. Unless the student obtains a completely unsatisfactory set of pH readings, which is highly unlikely, he should make only one NaOH vs. HCl titration. However, in Secs. 2·6 and 2·7, where accuracy was a primary concern, it was necessary to make several titrations so as to obtain a check on experimental precision.

Preliminary Operations: (a) There may be more than one type of pH meter in use in the laboratory. Carefully examine the one assigned to you, and refer to the instruction pages and the diagram for that pH meter, for directions as to the proper operating procedure (see Appendix). Caution: At all times when not in use the electrodes should be kept immersed in distilled water, so that the glass tip of the indicator electrode remains hydrated.

(b) Fill your burettes with the approximately 0.1 N NaOH and 0.1 N HCl solutions, following instructions given in Sec. 2·5 as to the proper way of rinsing and filling burettes. If the calomel reference electrode is not at least 1/3 full of saturated KCl solution, see the instructor for directions as to filling the electrode.

(c) Using the buffer solution furnished with the pH meter, standardize the pH meter according to the instrument directions in the

Appendix. Record in your notebook the nature of the buffer and its pH value. (Note: The supplied buffer solution is intended to suffice for the use of all students in the course; not just for you. Each pair of students at the same laboratory bench should share between each other, one small sample (about 50 ml) in one small beaker. Retain the portion of the buffer in the beaker until the end of the experiment; it may then be discarded.) You are now ready to continue to the titration.

Procedure for the pH titration of NaOH versus HCl: (Caution: During this titration do not allow the electrodes to remain in the strongly basic solution for prolonged periods of time; a strong base will etch the glass electrode and ultimately ruin it.)

(a) Set up data in your notebook as follows: (next page)

HCl, burette readings	pH reading	Additional directions and observations to be made
0.00 ml	________	
2.00	________	
10.00	________	
20.00	________	Add 2-3 drops of phenolphthalein solution at this point in the titration.
22.00	________	
23.00	________	
24.00	________	
24.20	________	Indicate with an arrow the reading where the pink color of phenolphthalein disappears.*
24.40	________	
24.60	________	
24.80	________	
25.00	________	**
25.20	________	To colorless solution, add 2-3 drops of mixed indicator solution.*
25.40	________	
25.60	________	
25.80	________	Indicate with an arrow the reading where the green color of the mixed indicator solution turns pink.*
26.00	________	
28.00	________	
30.00	________	
40.00	________	

*The indicators are added only for the purpose of showing that phenolphthalein changes in a basic solution, whereas the mixed indicator changes in an acid solution. If you missed color changes do not repeat the titration.

**This should be the true equivalence point, if the directions have been followed properly. The equivalence point occurs at the half-way point along the steep portion of the titration curve.

(b) Find in your notebook the HCl/NaOH volume-ratio with phenolphthalein indicator (procedure of Sec. 2·6). Divide your acid-base ratio, as obtained in that experiment, into the number 25.00. The result will be the number of milliliters of NaOH which are equivalent to 25.00 ml of your HCl solution.

For example, $$25.00\ \frac{\text{ml HCl}}{25.00\text{ ml HCl}} \div 1.014\ \frac{\text{ml HCl}}{\text{ml NaOH}} = 24.65\ \frac{\text{ml NaOH}}{25.00\text{ ml HCl}}.$$

Transfer the above amount of NaOH (25.00 divided by your acid/base ratio) from your burette into a 250 ml beaker. Place the beaker on a magnetic stirrer and add sufficient distilled water so that the fragile electrodes can be immersed in the solution without the possibility of being struck by the stirring bar. Immerse the (previously rinsed) electrodes. Turn on the stirrer, and gradually increase its speed until the middle range is reached.

(c) Arrange your burettes so that the one containing your HCl solution extends over the beaker. Run in the amounts of acid indicated in the table on the previous page. After each addition, allowing time for temperature equilibration, read the pH meter and record your observation.

(d) When you have finished, remove the beaker containing the titrated solution. Discard the solution and wash beaker thoroughly. Rinse off the electrodes and immerse them in a beaker of fresh, distilled water. Don't unplug the pH meter. Clean off the work space, and store the unused buffer solution, marking pencil, magnetic stirrer, and stirring bar where you found them.

Special Laboratory Report for the pH Meter Titration. Using graph paper supplied by the instructor, prepare a graph of your pH meter titration, plotting pH vertically and ml of titrant horizontally. Plot each pH as a point of the graph, and enclose each point in a small, neat circle. Using the data points as guides, draw a smooth curve for the complete titration. Label the graph clearly as to:

(1) Your name, and the date of the experiment,
(2) Solution being titrated,
(3) Titrant,

(4) Location of the true equivalence point, where the moles of added titrant exactly equals the moles of NaOH solution being titrated,

(5) Where each indicator changed color,

(6) What pH meter was used.

STANDARDIZATION OF ACID AND BASE SOLUTIONS

2·9 Preliminary Comments. A standard solution is one in which the concentration of the solute is known to a high degree of accuracy. In elementary quantitative chemistry, a student strives for an accuracy of 2 parts per thousand; therefore, the concentration of an approximately 0.1 N solution of base should be determined to within two parts in the fourth decimal place, e.g., for a solution whose actual concentration is 0.1098 N NaOH, determined values may fall between 0.1096 N and 0.1100 N and still provide the desired accuracy.

The standardization of a solution of base is usually accomplished by determining experimentally the volume of the base which is equivalent to a known weight of a pure acidic substance. Likewise a solution of an acid may be standardized by measuring accurately the volume of the acid that is equivalent to a pure basic substance. The extremely pure chemicals which are used for standardization are known as primary standards. Frequently, it is more convenient, in neutralization methods, to standardize either the base or acid solution against a primary standard, and then to determine the concentration of the other solution by means of a comparison of the acid to base volume-ratio (see Sec. 2·6 and Sec. 2·7). When a standard solution is used to determine the strength of another solution by means of a volume-ratio, the standard solution is referred to as a secondary standard. Theoretically a secondary standard is not as accurate as a primary standard, but in practice, the convenience may outweigh the inaccuracy of the method.

A primary standard is usually a solid substance about 99.95 per cent pure (impurity of 0.5 parts per thousand). It should be relatively soluble in water, and must react quantitatively with the solution to be standardized. The comparison of a satisfactory primary standard is not affected by drying, and ideally its equivalent weight should be fairly high in order that a large sample may be weighed without requiring more than a buretteful of solution in the standardization process.

Potassium acid phthalate ($KHC_8H_4O_4$) is the most widely used primary standard for the standardization of base solutions. Substances that are used to a lesser extent are potassium acid tartrate ($KHC_4H_4O_6$), potassium biiodate [$KH(IO_3)_2$], and sulfamic acid ($HSO_3 \cdot NH_3$).

For the direct determination of the normality of an acid, the recommended primary standard is anhydrous sodium carbonate with a purity of 99.95 per cent. Since it is impossible to purchase sodium carbonate commercially of this purity, it is general practice for analysts to prepare their own pure sodium carbonate from reagent grade sodium bicarbonate by prolonged heating at high temperature. Other substances which may be used as primary standards for the standardization of acid solutions are reagent grade calcium carbonate and mercuric oxide. These latter substances have the disadvantage of being insoluble in water; consequently, they must be dissolved in excess acid and back-titrated with standard base.

The authors have found that students secure more reliable results for the standardization of the HCl solution by means of acid-base ratios, using NaOH as a secondary standard than through the use of the primary standards mentioned above. However, the student should be aware of the possibility of direct titration of the HCl against a primary standard as a method for the standardization of this solution.

2·10 Standardization of Base Solutions.

Preliminary Operations: Pure potassium acid phthalate (frequently labelled potassium biphthalate) is to be found on the side shelf. Weigh approximately 4 grams of this substance, on a piece of glazed paper, and transfer to a clean weighing bottle. Your name should be marked with a graphite pencil on the ground glass portion of the bottle, with the letters KHP to identify the contained substance. Put the weighing bottle and material (with the bottom of the bottle cradled in the up-turned top) in the drying oven, and dry at 110°, for at least one hour. Stopper the bottle and place in the desiccator until needed.

Wash three wide-mouth, 500 ml, Erlenmeyer flasks, rinse with small portions of distilled water, and label flasks A, B, and C. The flasks need not be dried. Prepare a right-hand page of the notebook for recording the data of this experiment following the general form shown in Table 2·2. Proceed to the balance room with flasks, notebook, and desiccator containing the weighing bottle with the dry potassium acid phthalate.

Weighing the Samples: It is customary to handle a weighing bottle with a paper shield, i.e., a folded strip of paper encircling the bottle and held tightly to the body of the bottle by means of the ends of the strip.

The weighing bottle containing the dry material is first weighed, the weight recorded as in Table 2·2, and then the estimated amount of material is transferred, by cautious pouring, into the flask in which it is to be treated. The weighing bottle is closed and again weighed; the loss, or difference, in weight represents the sample taken. Four weighings are required for three samples. In the transfer of material, as described above, it is necessary that all of the sample leaving the bottle should be caught in the container. It is poor practice to return material from the receiving vessel to the weighing bottle since the receiving vessel is usually not dry. It is necessary for the student to learn by practice how to estimate the approximate sample weights.

Accurately weigh three samples to four significant figures (about 0.7 - 0.9 each) of pure potassium acid phthalate into the three labelled titration flasks. Record these weights and subsequent data in the notebook as indicated in Table 2·2.

Titrations: To each of the flasks add 75 ml of distilled water (measured in graduated cylinder) and 2-3 drops of phenolphthalein solution. Rotate flasks gently to hasten complete mixing.

Drain the water from burettes, rinse four times with the respective solutions to be used as instructed in Sec. 2·5, fill the burettes properly, take readings and record as indicated in Table 2·2. The acid solution is not used except for back-titration. However, the burette must be filled for each titration to avoid errors arising from lack of uniformity in the burette tube.

Place flask A under the NaOH burette, and add the base solution with rotation of the flask to insure mixing. The NaOH may be added rather rapidly as long as the pink color, produced on the first contact, fades quickly on mixing. When the color commences to disappear more slowly, decrease the rate of titration and finally complete it drop by drop, seeking a dead stop end point. Stop at the usual phenolphthalein end point, i.e., when a single drop produces a faint pink which lasts for as much as 15 seconds. Take the burette reading and record.

Back-titration: Should too much NaOH be added (over-titration), the situation may be saved by adding a measured volume of HCl for which you have an acid-base ratio from Sec. 2·6. After enough HCl has been added to make the solution colorless, proceed to the usual end point by drop-by-drop addition of the base. Sample C in Table 2·2 illustrates a hypothetical over-titration with proper calculations. The acid-base ratio is also hypothetical, and is the one given as an example in Table 2·1.

Results involving back-titrations are not as reliable as those secured with dead stop end points, because the former involves four burette readings for each result, whereas the latter involves only the two readings on the base burette. However, overly prolonged titrations allow carbon dioxide from the air to react with sodium hydroxide in the burette, with possible change in the normality of the base.

2·11 Standardization of Acid Solution by Comparison with Base Solution.

The most convenient method of standardizing the HCl solutions is through the use of the NaOH as a secondary standard in combination with the acid-base ratios. The hypothetical values indicated in Secs. 2·6, 2·7, and 2·10 will be used to illustrate this method.

In Sec. 2·6 and Table 2·1 the acid-base ratio (HCl/NaOH) with phenolphthalein as an indicator was assumed to have the value in 1.014. No value for the acid-base ratio with the mixed indicator, Sec. 2·7, was conjectured, but for the purpose of this explanation we will assume that a value of 1.019 was obtained. As was explained in Sec. 2·7, Table 2·2 Standardization of NaOH Solution with Potassium Acid Phthalate

Weighings:

	A	B	C
Wt. of KHP + bottle (before)	26.0297	25.3241	24.5764 g
Wt. of KHP + bottle (after removal of sample)	25.3241	24.5764	23.7941
Weight of samples:	0.7056	0.7477	0.7823

Burette readings:

A		B		C		
HCl	NaOH	HCl	NaOH	HCl	NaOH	
0.44	31.78	0.44	33.68	1.73	36.71	ml
0.44	0.26	0.44	0.36	0.44	0.56	
0.00	31.52	0.00	33.32	1.29	36.15	

(Hypothetical ratio of HCl/NaOH = 1.014 with phenolphthalein from Table 2·1)

General formula:

$$N = \frac{\text{Weight of sample of KHP}}{\text{ml of NaOH x milliequivalent weight of KHP}}$$

In case of back-titration:

$$N = \frac{\text{Weight of sample of KHP}}{[\text{ml of NaOH - (ml of HCl/ratio)] x meq. wt. of KHP}}$$

Calculations:

			Deviations:
Sample A	$N = \frac{0.7056 \text{ g}}{31.52 \text{ ml x } 0.2042 \text{ g/meq}}$	= 0.1096 meq/ml	0.0002
Sample B	$N = \frac{0.7477}{33.32 \text{ x } 0.2042}$	= 0.1099	0.0001
Sample C	$N = \frac{0.7823}{[36.15 - (1.29/1.014)] \text{ x } 0.2042}$	= 0.1098	0.0000
	Average	= 0.1098 N	0.0001

Therefore the normality of the hypothetical base = 0.1098 N these ratios are necessarily different. Consequently, the normality of the HCl will have two values; one value when used with phenolphthalein as an indicator, and the other value when used in titrations in which the mixed indicator solution is involved. Using the values assumed in the preceding sections we can arrive at the following normalities for HCl:

With phenolphthalein: (See Sec. 2·6) $\frac{\text{Normality of base}}{\text{HCl/NaOH ratio}} = \frac{0.1098}{1.014} = 0.1083\text{ N}$

With mixed indicators: (See Sec. 2·7) $\frac{\text{Normality of base}}{\text{HCl/NaOH ratio}} = \frac{0.1098}{1.019} = 0.1078\text{ N}$

The student must realize that all of the values given in the preceding sections are merely illustrative for the purpose of explaining how acids and bases may be standardized. The student's experimental values may vary considerably from those used in the examples.

Important: In the exercises involved in the analyses of unknown acids and bases, which are given in this chapter, the student will use the normality of the acid (with phenolphthalein) only in back-titrations involving the determination of the percentage composition of an unknown acid sample. The normality of the acid (with mixed indicator) is used in the analysis of impure soda ash.

ANALYSES OF ACID AND BASE SAMPLES

2·12 Preliminary Comments. In the analyses of acid samples the instructor has a choice of giving the student pure solid acids or acid salts for the determination of equivalent weights, or requiring the analyses of impure acids for percentage compositions.

Among the solid acids and their acid salts which may be obtained in a degree of purity necessary for equivalent weight determination, a few may be listed as follows: succinic acid, benzoic acid, oxalic acid, sulfamic acid, potassium bioxalate. Any of these substances can be issued as solid unknowns from which weighed samples may be titrated with standard NaOH to secure equivalent weight values. The general formula is as follows:

$$\text{Equivalent weight} = \frac{(\text{weight in grams of the acid}) \times (1000\text{ mg/g})}{(\text{ml of NaOH used}) \times (\text{N of NaOH})} = \frac{\text{mg}}{\text{meq}}$$

However, the widely differing equivalent weights of these substances creates a problem for the instructor in writing up laboratory procedures which can be used in highly precise equivalence determinations for a variety of the compounds. For example, a sample of oxalic acid would require approximately six times the volume of standard base as would be required by the same weight of potassium biiodate.

The instructor usually finds the most satisfactory solution to the problem of acid analysis is the use of samples of impure potassium acid phthalate. Such samples are commercially available, in varying percentage compositions which have been determined by professional analysts. A procedure for the analysis of potassium acid phthalate samples containing known quantities of inert materials is given in Sec. 2·13.

Very few substances are satisfactory as unknowns for student analysis of base constituency. However, certain carbonates, particularly sodium carbonate and calcium carbonate, have been used quite successfully as unknown samples in elementary quantitative analysis. Sodium carbonate is more desirable since it is water soluble, whereas calcium carbonate is not. Commercial samples of sodium carbonate are available containing known quantities of inert materials. Usually the combination of sodium carbonate with an inert material is designated as soda ash, and the procedure for the analysis of such samples is contained in Sec. 2·14.

Although the particular choices of acid-base unknowns used in exercises 2·13 and 2·14 are dictated by the academic considerations above, it should be emphasized that comparable acid-base analyses are encountered in research and quality control laboratories throughout the world. There the analytical chemist is faced with the additional problems of selecting the size of sample to use, the best indicator for the analysis, the appropriate concentrations for the titrants, etc. -- problems which, for lack of student laboratory time, have already been answered for you in these particular exercises.

2·13 Analysis of an Acid Sample.

Principles: The equivalent weight of any acid may be calculated by dividing the formula weight of the acid by the number of protons (customarily referred to as hydrogen ions) furnished by each acid molecule or formula group in the reaction. For potassium acid phthalate, which yields one proton per hydrogen-phthalate ion, the equivalent weight is (the formula weight)/1.

A gram equivalent weight (or an equivalent) of an acid is that quantity of acid which furnishes a mole of protons (1.008 grams of protons). An equivalent of acid will neutralize an equivalent of base (e.g., 40.01 g of solid sodium hydroxide or one liter of a normal solution of sodium hydroxide). Similarily, a milliequivalent of acid will neutralize a milliequivalent of base (e.g., one ml of a normal solution of base). A general relationship may be written: (ml of titrant x N of titrant) = $\frac{\text{wt. of pure sample (in grams)}}{\text{milliequivalent weight of sample (in g/meq)}}$

The present exercise is concerned with the analysis of a known acid (potassium acid phthalate with an equivalent weight of 204.2, or 0.2042 g/meq) of unknown purity. The general formula for calculating the per cent purity of the acid is:

$$\text{\% of pure acid} = \frac{\text{the weight of pure acid as determined by titration}}{\text{the total weight of impure acid}} \times 100$$

$$= \frac{\text{(ml base x N base) x milliequivalent wt. of acid}}{\text{weight of impure sample in grams}} \times 100$$

Therefore,

$$\text{\%KHP} = \frac{\text{(ml NaOH x N NaOH) x 0.2042 g KHP/meq x 100}}{\text{g of impure KHP}}$$

Note that this formula is merely a modification of that given in Sec. 2·12 for determining an unknown equivalent weight for a pure acid.

Procedure: Secure an unknown sample from the instructor, and dry it in an oven at 110° C for a period of at least an hour. The dried sample is permitted to cool (in desiccator) for approximately 20 minutes. It is acceptable practice to always store dried samples (in weighing bottles) in the desiccator except when portions are being weighed.

Proceed to the analytical balance with the dried unknown (in desiccator), and weigh accurately (to 0.1 mg), three samples of approximately one gram each, into plainly marked 500 ml wide-mouth Erlenmeyer flasks. Record the weighings and the subsequent titrations, as well as the calculations pertaining to them, in much the same manner as the sample data shown in Table 2·2.

By means of a graduate, add 75 ml of distilled water to each sample, and dissolve the samples by gentle rotation of the flasks. Add 2-3 drops of phenolphthalein indicator solution, and titrate with your standard NaOH solution, seeking a dead-stop end point. Calculate the results according to the formula given in this section for obtaining the percentage composition of impure potassium acid phthalate.

If the end point is overstepped, add a measured volume of standard HCl from the acid burette until the solution is colorless, and then complete the titration with NaOH. Subtract the milliequivalents of HCl used in the back-titration from the total milliequivalents of NaOH necessary for the titration. In a calculation of this kind the formula on the preceding page is modified to the following:

$$\frac{[(\text{ml of NaOH} \times N) - (\text{ml of HCl} \times N)] \times 0.2042 \text{ g/meq} \times 100}{\text{Weight of sample in grams}} = \% \text{ of KHP}$$

Precision: With careful work a student should be able to attain a precision of 2 or 3 parts per thousand for the analytical results of the foregoing analysis. A precision of more than 5 parts per thousand would indicate that additional samples should be analyzed. Note that errors in weighing, as well as errors in titration, may produce imprecise and inaccurate results.

Report: The report (for this unknown and all future analyses) should be submitted on a loose sheet of paper, 8 1/2 x 11 inches in size. It should be a copy of the weighings, titrations, and the set-up for the calculations pertinent to the analysis. These details should be entirely complete, and in a neat, tabular form. All such reports will be retained by the instructor in case future reference to them is necessary.

2·14 Analysis of a Base Sample.

Principles: Soda ash (impure sodium carbonate) is used as an unknown substance for student determinations because it is a typical solid of an alkaline material, and offers an exercise in the use of mixed indicators and in back-titration. Because of the physical nature of soda ash it is sometimes difficult to obtain samples of a high degree of homogeneity. Even so, it seems preferable to weigh out individual samples of this material rather than large samples for use in "aliquot portion" techniques as described in many laboratory procedures.

The formula weight of sodium carbonate is 106.00. Since each carbonate ion reacts with two hydronium ions, according to the equation:

$$CO_3^{=} + 2\ H_3O^+ \rightarrow 2\ H_2O + CO_2,$$

the equivalent weight of sodium carbonate is one half of the formula weight, or 53.00. Consequently, the milliequivalent weight of sodium carbonate is 0.05300 (units: g/meq). The end point in a soda ash titration is reached by first adding an excess of acid titrant and then back-titrating with base titrant; therefore, it is necessary to subtract the milliequivalents of base titrant from the total milliequivalents of acid titrant used for the soda ash. The resulting formula for analysis of an impure sample of Na_2CO_3 is:

$$\%Na_2CO_3 = \frac{\text{determined weight of pure } Na_2CO_3}{\text{total weight of impure } Na_2CO_3} \times 100$$

$$= \frac{(\text{net meq acid used}) \times 0.05300 \text{ g/meq} \times 100}{\text{g of impure sample}}$$

$$= \frac{[(\text{ml HCl} \times \text{N HCl}) - (\text{ml NaOH} \times \text{N NaOH})] \times 0.05300 \text{ g/meq} \times 100}{\text{g of impure sample}}$$

The normality of the HCl used here is that obtained with mixed indicator solution.

Procedure: Weigh, to the nearest tenth of a milligram, three samples of soda ash (properly dried in oven) of about 0.4 gram each, and place each sample in a clean 500 ml Erlenmeyer titration flask, marking each flask for identification as A, B, and C. Dissolve each sample in about 50 ml of distilled water.

Add 1 drop of methyl orange indicator to sample A and titrate with standard HCl until a definite color change is obtained, and then add 1 ml in excess. Record original burette readings, but do not make a final burette reading at this point since more acid is required to complete the titration.

Place the flask on a wire gauze, and heat over a free flame until the solution barely comes to a boil, then continue to boil gently for 1 minute to evolve the carbon dioxide liberated from the sample. Cool, by means of tap water on side of flask, add 2-3 drops of bromcresol green--methyl red indicator, and titrate slowly with standard NaOH solution until a green color is obtained. Now back-titrate with acid to a pink color, then add base dropwise until one drop gives a sharp change to green. It is advisable to approach the end point by addition of base in each titration. Read both burettes, and record final readings. Keep records as in preceding sections.

Titrate samples B and C in like manner, and record the results of your titrations. From the net milliequivalents of acid used, and the weights of the unknown samples calculate the percentage of Na_2CO_3 in the original material, as indicated under principles in this section. To repeat, it is essential that the normality of the acid be that obtained with mixed indicator solution.

The agreement of values between samples A, B, and C should be within 4 parts per thousand. If not, additional samples should be determined. Fill out a complete report sheet as in unknown No. 1.

SUMMARY

Neutralization methods, frequently designated as acidimetry and alkalimetry, are used throughout the entire field of chemistry. It is impossible to find any segment of chemistry, be it organic, inorganic, analytical, physical, biochemical, industrial, or any other branch of chemistry, which does not depend upon neutralization methods for some purposes of control and research.

Most acid-base reactions take place in water solutions; however, many other solvents have been used as reacting mediums for such reactions. The equilibrium of the hydroxide and hydronium ions in water is a controlling factor of many chemical processes. Topics relating to acidimetry and alkalimetry are too numerous to be listed in this summary; however, any chemistry-oriented student is urged to supplement his experiences in these exercises by additional readings in more advanced texts.

Chapter 2 includes only the minimum essentials for the introduction of neutralization methods for a one-semester course in quantitative chemistry. Two important analytical tools, the volumetric burette and the pH meter, have been introduced with appropriate experimentation to indicate their importance. The burette is the most widely used implement of titrimetric methods, whereas the pH meter has a variety of uses in graphical analyses. Both tools will be involved in later experiments.

Chapter 3

REDOX METHODS

PERMANGANATE PROCESSES

3·1 Preliminary Comments. Many ions may be quantitatively oxidized or reduced on a variety of analytical processes. The variety is so great that it is impossible to examine them in an elementary course. It may suffice to state that redox methods are more widely used than all other volumetric methods combined.

Important oxidizing agents, which are frequently used in standard solutions include potassium permanganate, potassium dichromate, ceric ammonium sulfate, iodine, and potassium iodate. Reducing agents used in the form of standard solutions include sodium oxalate, sodium arsenite, ferrous ammonium sulfate, and sodium thiosulfate.

Potassium permanganate is probably the most widely used of all volumetric agents. It is a versatile reagent in that it may be used to determine many substances by direct or indirect titrations, and may be controlled to produce products in several oxidation states. It also has the peculiar advantage over most other titrants in that the highly colored MnO_4^- ion serves as its own indicator.

Several disadvantages attend the use of permanganate solutions, which are listed as follows:

(1) In preparing $KMnO_4$ solutions it is necessary to remove MnO_2, by filtration, which may be present as an impurity in the reagent, or which may be formed by a reaction between MnO_4^- and impurities in distilled water. The presence of MnO_2 catalyzes the decomposition of $KMnO_4$ solutions.

(2) An aqueous solution of permanganate is not completely stable because of the tendency of the ion to oxidize water and traces of organic material in distilled water to produce MnO_2 and oxygen. Although this decomposition reaction is fairly slow it may necessitate the occasional restandardization of the solution.

(3) There is a tendency for the permanganate ion to oxidize the chloride ion when hydrochloric acid occurs in a titration mixture as a preliminary solvent.

(4) There are numerous possible reaction products in permanganate oxidation unless the titrations are carried out under rigorous, specified conditions.

In spite of the disadvantages recognized as occurring with the use of MnO_4^- as an oxidizing agent, many determinations have been extensively studied and have been found to be highly accurate when properly performed.

3.2 Preparation of Approximately 0.1 N $KMnO_4$. In a strongly acid solution the permanganate ion is reduced to the manganous ion according to the following half-reaction:

$$MnO_4^- + 8\ H^+ = Mn^{++} + 4\ H_2O$$

Such a solution is a powerful oxidizing agent, with a standard oxidation potential of -1.52 volts. Five electrons are required in the redox process indicating that the equivalent weight of potassium permanganate is one-fifth of its formula weight.

$$KMnO_4/5 = 158.04/5 = 31.61$$

To prepare a 0.1 N $KMnO_4$ requires one-tenth of the equivalent weight in grams of the reagent dissolved in sufficient water to produce one liter of solution.

Using a laboratory trip-beam balance, weigh on a watch glass a 3.25 gram portion of $KMnO_4$ crystals. Divide roughly, half-and-half, between two clean 600 ml beakers, and add approximately 500 ml of distilled water to each. Cover beakers with 6 inch watch glasses and heat to boiling. Place the hot solutions, still covered inside the desk for a period of at least 24 hours.

As part of the same work, clean with chromic acid cleaning solution a 500 ml side-arm filtering flask, and a one liter glass-stoppered bottle. After cleaning and thoroughly rinsing, leave these containers in a suitable position to drain for 24 hours.

Before storing away the filter flask prepare a Gooch crucible with an asbestos mat of approximately 1.5 mm thickness. To prepare the mat, shake the shelf-reagent bottle containing asbestos soup (a mixture of water and a small amount of acid-washed asbestos fibers), then pour the soup into the crucible, with suction partly on, as indicated in Fig. 3·1. While the soup is passing through the crucible, tamp the mat into formation with a stirring rod whose ends have been well-rounded by fire polishing. A properly prepared mat can be distinguished by looking through the crucible toward a strong light. If no light can be seen, the mat is too thick. If the holes of the crucible are visible the mat is too thin. If a small amount of light can be observed through the mat it is of suitable thickness.

After 24 hours, or more, have elapsed the permanganate solution may be filtered. In filtering the solution arrange the Gooch crucible as shown in Fig. 3·1. Be certain to insert a safety bottle between the filter flask and the aspirator, otherwise tap water may be sucked accidentally into the filtered permanganate. It will be necessary to empty the filtering flask several times during the filtration.

Store the filtered permanganate solution in a clean one-liter glass-stoppered bottle, and keep in the dark when not in use. When properly prepared, and protected from heat and light, the solution is sufficiently stable for quantitative work over a period of several weeks. Any decomposition can be recognized by the deposition of a brown coating of MnO_2 on the walls and bottom of the storage bottle.

3·3 Standardization of $KMnO_4$ Solution. Potassium permanganate is not available in sufficient purity to be weighed directly as a standard. It is customary to prepare an approximately 0.1 N solution, and then titrate the solution against a primary standard (see Sec. 2·9). The most frequently used standards are sodium oxalate, arsenious acid, and iron wire. Of these, sodium oxalate, of a high degree of purity, is the most satisfactory for student use. The overall reactions of permanganate with sodium oxalate are given in the following equations:

$$2\,Na^+ + C_2O_4^{=} + 2\,H^+ = H_2C_2O_4 + 2\,Na^+$$

$$2\,MnO_4^- + 5\,H_2C_2O_4 + 6\,H^+ = 2\,Mn^{++} + 10\,CO_2 + 8\,H_2O$$

Weigh out to the nearest 0.1 mg three samples, between 0.2500 and 0.3000 g, of previously dried $Na_2C_2O_4$, and transfer the samples to wide-mouth 500 ml Erlenmeyer flasks (properly identified). Dissolve each sample in a solution of 100 ml of 1.5 N H_2SO_4 (prepared by dissolving 13 ml of concentrated H_2SO_4 in 300 ml of water).

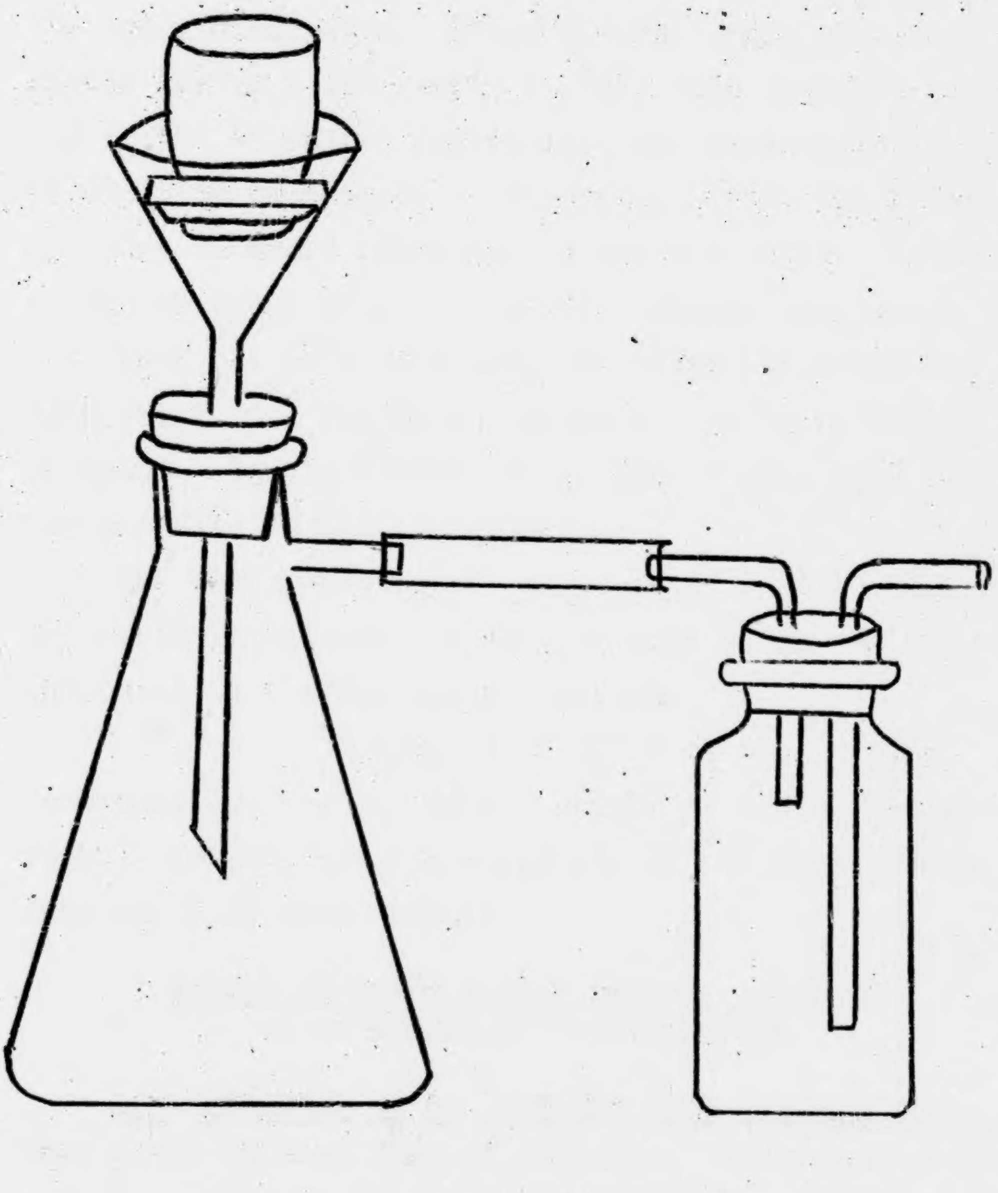

Fig. 3·1 Filtration of permanganate solution through Gooch crucible.

Heat the solution to a temperature between 80 and 90° C, measured with a thermometer. Once introduced into the flask, the thermometer must not be removed until the titration is completed. Titrate with permanganate with constant swirling, but be certain that the temperature is maintained above 70° C at all times. At first the permanganate should be added drop by drop, with swirling after each addition until the color disappears. After several drops have been added the permanganate may be added fairly rapidly with constant swirling. Toward the end of the titration particular care must be taken to allow the color, produced by each drop, to disappear before the addition of the next, in order to avoid overstepping the end point. Titrate to the first permanent faint pink color, which should last about 15 seconds.

From the data obtained, calculate the normality of the permanganate solution. Duplicate values should check within two parts in one thousand. If the average deviation is more than four parts per thousand the exercise should be repeated.

The half-reaction of oxalic acid (derived from sodium oxalate) involves two electrons for each formula weight of the oxalic acid, as is indicated in the following equation:

$$H_2C_2O_4 = 2\,H^+ + 2\,CO_2 + 2\,e^-$$

Consequently, the equivalent weight of sodium oxalate is one-half of its formula weight, and the normality of the permanganate may be obtained from the following formula:

$$\frac{\text{Weight of dried sodium oxalate in grams}}{\text{ml of } KMnO_4 \times 0.06700 \text{ g/meq}} = \text{N of } KMnO_4 \text{ solution}$$

3·4 Analysis of an Iron Ore with Permanganate. The principal iron ores occur in some form of an oxide. Treatment of the ore in the determination of iron consists of three separate steps: (1) solution of the sample; (2) reduction of the dissolved iron to the ferrous state; and (3) titration of the ferrous ions to the ferric state with standard permanganate. A number of precautionary measures are necessary within each step. These measures are included and explained within the detailed procedure for the analysis.

After a portion of the ore has been dried for an hour or more, at 110° C, weigh three samples accurately on the analytical balance. The weights of the samples should fall between 0.3000 and 0.4000 g. Transfer the weighed samples to 500 ml wide-mouth Erlenmeyer flasks, and dampen each sample with a few drops of distilled water. The purpose of the moistening is to prevent any loss of the finely divided powder.

Add 15 ml of concentrated hydrochloric acid to each sample; cover with watch glasses, and heat gently with an open flame (PERFORM THIS OPERATION IN A HOOD) until the samples are disintegrated as indicated by the disappearance of all dark particles of the original sample. Keep the volume fairly constant by additions of distilled water, if necessary. The solution process usually requires about 30 minutes. When disintegration is complete there may be a residue of white or gray siliceous material, but such a residue is to be ignored. The resulting solution is yellow in color and contains a mixture of ferrous and ferric ions. The latter is probably a chloride complex with a formula of $FeCl_4^-$.

The following procedure is to be followed for each sample individually, from stannous reduction through the permanganate titration, because ferrous ions are not stable over an extended period:

Heat the individual sample nearly to boiling, and add stannous chloride solution dropwise until complete reduction of ferric ions is accomplished as is indicated by the disappearance of the yellow color. However, there may remain a faint greenish-blue color which is characteristic of the ferrous ion. Avoid an excess of more than two drops of stannous chloride. The equation for the stannous reduction is as follows:

$$2\ FeCl_4^- + Sn^{++} = 2\ Fe^{++} + SnCl_6^{=} + 2\ Cl^-$$

Cool the flask completely by running cold water over the outside of the container, and without delay add rapidly 25 ml of mercuric chloride solution. (If the reagent is not added rapidly, a local excess of stannous ions may cause the reduction of $HgCl_2$ to Hg instead of Hg_2Cl_2.) A small white silky precipitate of mercurous chloride should result. If the solution is gray or dark in color it should be discarded. If there is no precipitate, insufficient stannous chloride was used, and such a solution should likewise be discarded. The purpose of adding the mercuric chloride is to destroy excess stannous ions:

$$Sn^{++} + 2\,HgCl_2 + 4\,Cl^- = SnCl_6^{=} + \underline{Hg_2Cl_2}$$

Dilute the solution to approximately 300 ml with distilled water, and then add 25 ml of preventive (Zimmermann-Reinhardt) solution. This solution contains a mixture of manganous sulfate, phosphoric acid and sulfuric acid. The manganous sulfate lowers the oxidizing potential of the permanganate-manganous system and thereby inhibits the possible oxidation of the chloride ion. Phosphoric acid forms a colorless complex phosphate with ferric ions, possibly $Fe(PO_4)_2^{---}$, and thus prevents the formation of yellow $FeCl_4^-$ ions during titration, which would obscure the permanganate end point.

Titrate immediately with standard permanganate solution, with constant whirling of the flask, to the appearance of a faint pink color which remains for 15 seconds. Rapid titrations give more accurate results by decreasing the likelihood of side reactions.

Compute and report the average percentage of Fe in the iron ore. The results should agree within three parts per thousand. The formula for the calculation is as follows:

$$\frac{(\text{ml of } KMnO_4 \times N) \times 0.05585 \text{ g/meq Fe} \times 100}{\text{weight of sample in grams}} = \%\text{ of Fe in ore}$$

3·5 Techniques of Filtration with Filter Paper. The use of filter paper is usually restricted to gravimetric procedures in which a substance is precipitated, washed, then ignited to constant weight. However, the determination of calcium by indirect analysis with standard permanganate, as given in Sec. 3·6, is a useful volumetric determination, which requires quantitative precipitation and subsequent quantitative filtration of calcium ions as calcium oxalate, prior to volumetric titration.

Most quantitative filtrations require 11 cm, acid-washed, papers that may be procured in coarse, medium or fine porosities. This size filter paper is customarily fitted into a fluted glass funnel, which has an angle of 60 degrees and a diameter of 65 mm.

The process of folding the filter paper and fitting it into a funnel involves essential but simple techniques. As indicated in Fig. 3·2, the filter paper is folded along its diameter, and again along the radius at nearly right angles to the first fold. A cone is formed, when opened, which has an angle of 60 degrees. Moisten the cone and insert it securely into a fluted funnel. Using the fingers, press the top part of the paper into close contact with the funnel. (Older procedures have suggested that the outer top corner of the cone be torn off to speed up filtration. This is a questionable procedure which is quite unnecessary with fluted funnels.)

Place the properly prepared funnel and filter paper in a slot of a wooden funnel support, with the receiving beaker underneath. It is good technique for the stem of the funnel to touch the receiving vessel to avoid spattering.

In a quantitative precipitation the precipitate usually is aged by standing to increase crystal size; the liquid above the precipitate is called the supernatant liquid. After proper ageing (or digesting) the supernatant liquid is poured cautiously down a stirring rod, Fig. 3·3, taking care that the level of the liquid does not come within 1/4 inch of the top of the filter cone. As far as possible keep the bulk of the precipitate in the beaker. A precipitate on a filter paper cannot be washed as thoroughly, or as rapidly, as in the beaker.

To minimize solubility losses, the precipitate should be washed with the smallest practical quantities (usually 10-15 ml) of liquid. During each washing, stir the precipitate with the liquid in the original precipitation beaker, and allow to settle; then pour the supernatant liquid through the filter, still seeking to keep the bulk of the precipitate in the beaker. Usually five washings are sufficient.

3·6 The Determination of Calcium in $CaCO_3$ with Permanganate Solution. A weighed sample of impure calcium carbonate is dissolved in acid, and the calcium is precipitated as insoluble calcium oxalate by the addition of ammonium oxalate and ammonia. The precipitated calcium oxalate is filtered quantitatively and washed free of excess oxalate. It is then dissolved in dilute sulfuric acid, and the resulting solution titrated with standard permanganate. The amount of permanganate required to oxidize the oxalate is a measure of the total calcium. The

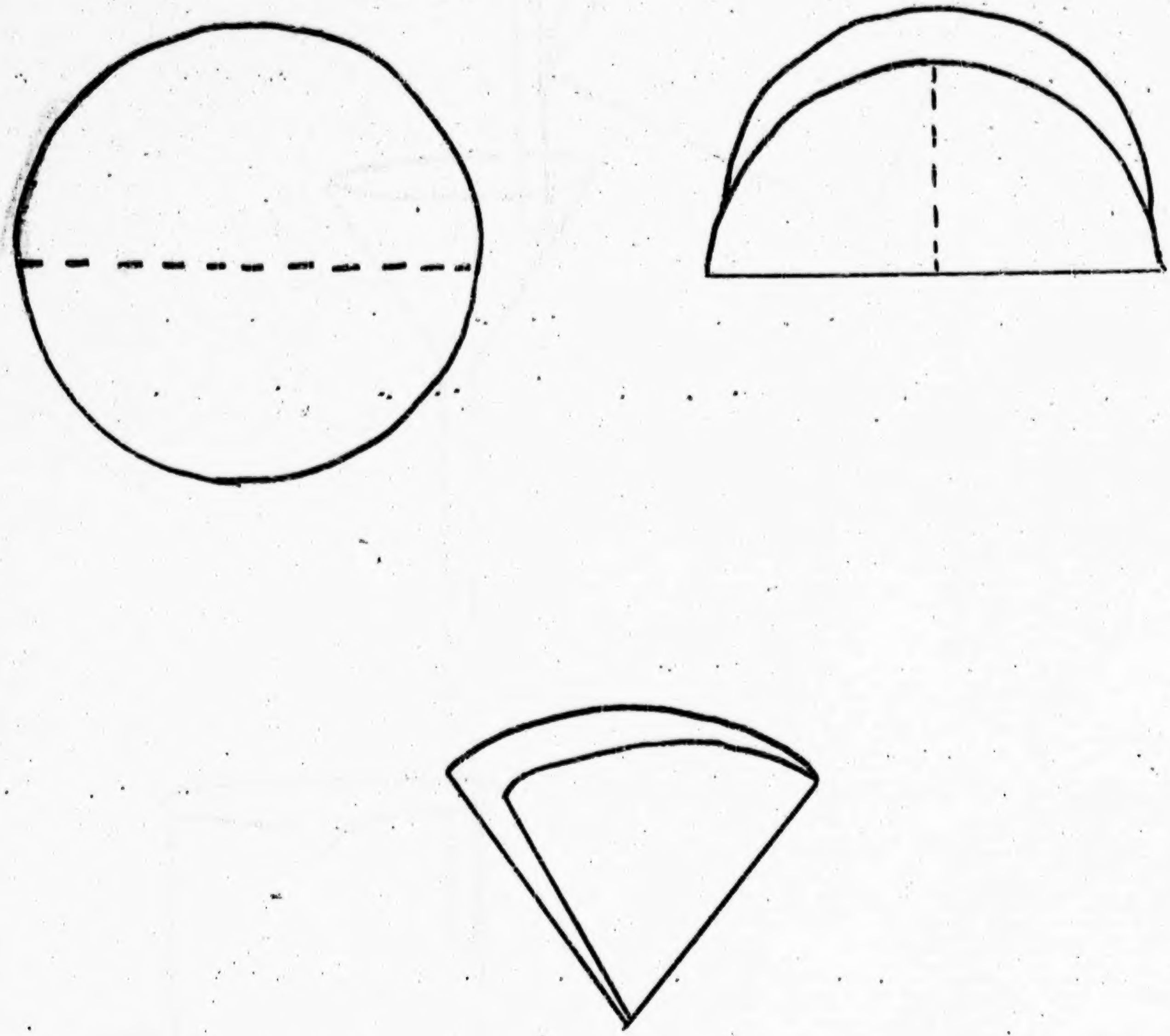

Figure 3·2 Folding a filter paper.

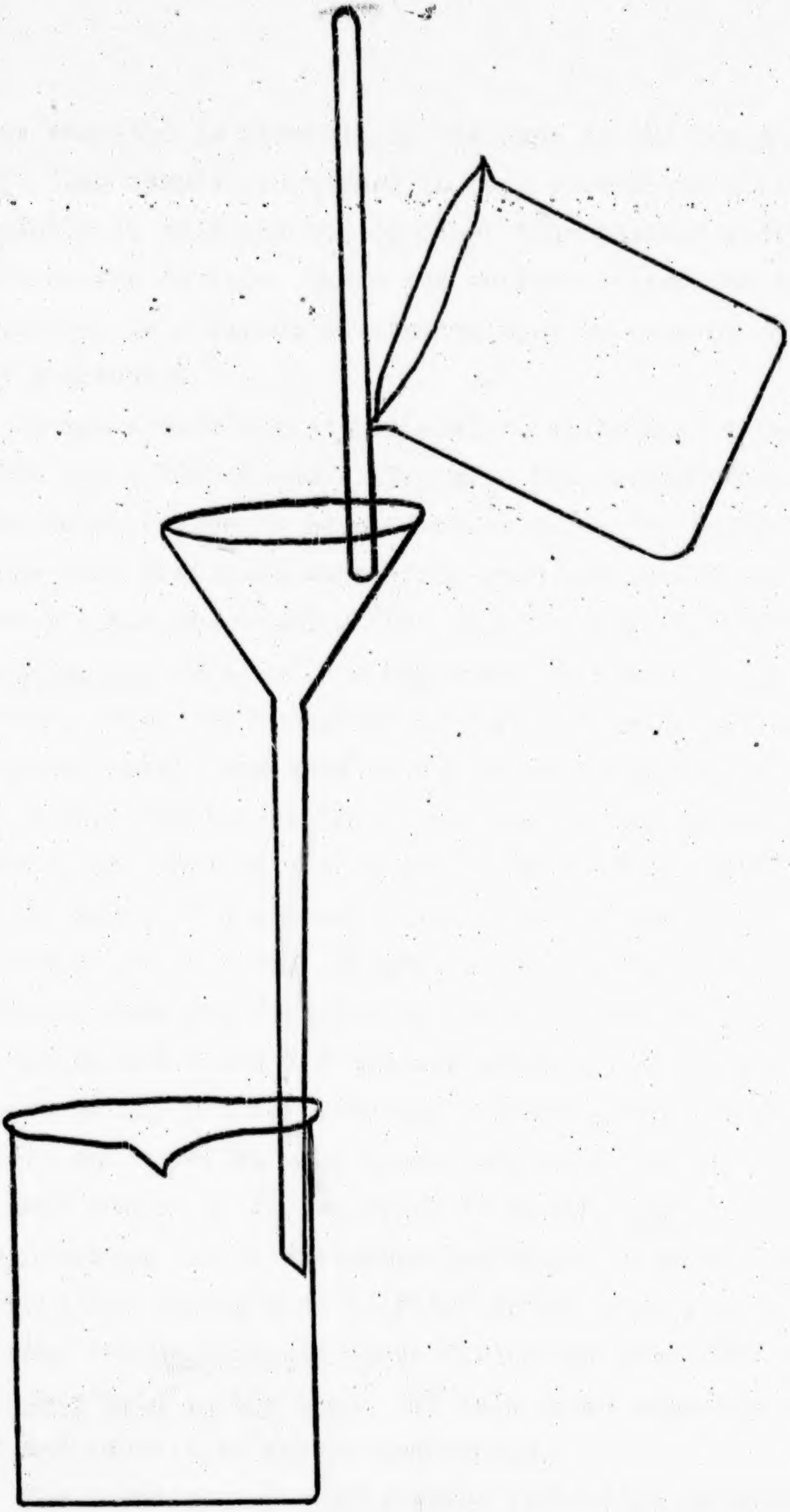

Figure 3·3 Technique of quantitative filtration.

redox reaction is essentially the same as the one given in Sec. 3·3. Note. The samples furnished in this experiment contain no material insoluble in acid and no ion other than calcium which can be precipitated as the oxalate. When the method is used for the analysis of native limestone, interfering substances must be removed by lengthy preliminary procedures.

Weigh accurately on the analytical balance three samples between 0.3000 and 0.4000 g each. Transfer the weighed samples to 400 or 600 ml beakers, (properly identified, e.g., A, B, and C) and dampen each sample with distilled water from wash bottle. Cover each beaker with a watch glass, and, taking care to avoid loss by effervescence, introduce approximately 10 ml of 6 N HCl under each watch glass with the aid of a pipette. When the evolution of carbon dioxide has ceased, add 10 ml of distilled water, and warm gently if necessary to effect complete solution. Wash down, into the beakers, anything on the underside of the cover glasses, and then dilute to about 200 ml with distilled water.

By means of a graduate add to each beaker 20 ml of 0.25 M ammonium oxalate solution. Heat to gentle boiling and, if any precipitate or turbidity remains, dissolve by the cautious addition of 6 N HCl. To the hot solution add 6 N ammonia gradually until a strong odor of ammonia persists after stirring. Leaving the stirring rods in the beakers and covering each beaker with a watch glass, set aside until the next period or for at least 18 hours. Note. In every quantitative precipitation, it is customary technique to provide each beaker with a stirring rod having fire-polished ends. Once placed in the solution, a stirring rod must remain there during the remainder of the analysis except when held in the hand. If laid down, adhering material will be lost and impurities may be introduced.

The technique of quantitative filtration is discussed in Sec. 3·5, which should be read carefully before continuing the calcium determination.

Only quantitative filter paper of medium porosity, e.g., Whatman No. 40, should be used for filtering the calcium oxalate precipitate. Obtain this paper from your instructor. (Quantitative filter paper is quite expensive and, to avoid waste, is not issued in the desk kit.)

Observing all the precautions explained in Sec. 3.5, filter the solution from the precipitation sample A through 11 cm quantitative filter paper in a fluted glass funnel. (Each funnel is identified for each precipitate, e.g., A, B, and C, and supported on a funnel rack over containers to receive the supernatant liquids and washings. Never use suction with filter paper.) Samples B and C may be filtered simultaneously with A through two other filters. As far as possible leave the precipitates in the original beakers. When all of the liquids have passed through the filters, discard the water-clear filtrates. Wash the precipitates repeatedly with small (10-15 ml) portions of cold distilled water containing a few drops of ammonia water. After three or four washings, test the filtrate for the oxalate ion. Continue the washing until a 10 ml portion of the last filtrate gives no test for the oxalate. (Too many washings will dissolve a precipitate and cause the analysis to run low.) Note. Test for the oxalate ion in the washings as follows: Collect approximately 10 ml of the filtrate in a test tube, add 1 ml of 3 N H_2SO_4, and heat nearly to boiling; then add one drop of potassium permanganate solution. If the pink color remains, the absence of the oxalate is confirmed. As long as the pink color is bleached, the washing should be continued.

When the test for the oxalate ion is negative, remove the filter paper from the funnel and place it, with its contents, in the original beaker containing the bulk of the precipitate. By means of a graduated cylinder, add 100 ml of 3 N sulfuric acid* and warm gently with stirring to dissolve the calcium oxalate. Dilute with 100 ml of distilled water, and heat nearly to boiling. Titrate the hot solution with standard permanganate. The presence of the quantitative filter paper will not interfere with the end point reading.

It is customary to calculate calcium in terms of CaO, which has a milliequivalent weight of 0.02804. The formula for the calculation is given as follows:

$$\frac{(\text{ml of } KMnO_4 \times N) \times 0.02804 \text{ g/meq} \times 100}{\text{weight of sample in grams}} = \%\text{ of CaO}$$

*Note. If the sulfuric acid is a great deal stronger than 3 N, it will cause the potassium permanganate to oxidize the filter paper; consequently, the analysis will not be reliable.

SOME IODINE PROCESSES

3·7 Preliminary Comments. Iodine is a weak oxidizing agent as compared with potassium permanganate. It can react quantitatively only with substances which are active reducing agents. Among the limited number of substances which can be oxidized quantitatively with iodine are H_2S, $H_2AsO_3^-$, and H_2SO_3. On the other hand, the iodide ion may be readily oxidized to molecular iodine by most strong oxidizing agents. The use of iodine methods is largely due to the fact that starch in an iodine-iodide system is the most sensitive visual indicator in quantitative chemistry.

Since iodine may be either reduced or produced by oxidation, there are two different types of iodine methods, direct and indirect. The use of iodine as a direct titrating agent is known as the iodimetric method, whereas the production of iodine by iodide ion to iodine is designated as the iodometric method. Typical examples are:

Iodimetric Method: $H_2AsO_3^- + I_2 + H_2O = H_2AsO_4^- + 2\,I^- + 2\,H^+$

Iodometric Method: $2\,Cu^{++} + 4\,I^- = 2\,\underline{CuI} + I_2$

However, neither of the foregoing reactions are necessarily quantitative. The first reaction must be driven to completion by the addition of bicarbonate ions to remove the hydrogen ions; and in the second reaction, the liberated iodine must be titrated by standard thiosulfate solution.

The titration of iodine against sodium thiosulfate, with starch as an indicator, is extremely accurate. In fact, the thiosulfate ion cannot be titrated quantitatively by any reagent other than iodine. This fundamental reaction takes place only in slightly acid or neutral solutions. The equation is as follows:

$$2\,S_2O_3^{=} + I_2 = S_4O_6^{=} + 2\,I^-$$

The reaction is reversible, making it possible to back-titrate an overstepped end point with the opposite solution. The reversibility also permits the secondary standardization of one solution when the other solution has been standardized against a primary standard. It is usually customary to standardize iodine solution against arsenious oxide, and then to standardize the thiosulfate solution against the iodine solution by the ratio value for the two solutions.

3·8 The Preparation of Approximately 0.1 N Iodine Solution. Iodine is relatively insoluble in water, but dissolves readily in potassium iodide solution due to the formation of the complex I_3^- ion. The highly reversible reaction is indicated by the equation,

$$I_2 + I^- = I_3^-$$

However, the rate with which iodine dissolves in KI is slow, and particularly so if the iodide concentration is low. It is common practice to dissolve the iodine in a concentrated iodide solution, and then dilute to the desired volume. Extreme care must be taken to be certain that all of the iodine is dissolved before dilution, otherwise, the normality of the resulting solution will increase as the undissolved iodine eventually dissolves.

Procedure. Weigh out 30 g of potassium iodide, on glazed paper using a triple beam balance, and dissolve in 15 ml of distilled water contained in a 150 ml beaker. Also weigh out 9.8 g of reagent-grade iodine, on a watch glass, using the rough balance. Add the iodine to the potassium iodide solution, and stir until the iodine is completely dissolved. (Examine by looking upward through the bottom of the solution.) After the solution is complete, transfer to a glass-stoppered one-liter bottle, and dilute to approximately 750 ml. (A 250 ml volumetric flask may be used for measuring 750 ml of distilled water in the dilution.) Mix thoroughly, store in the dark, and let the solution stand for at least 24 hours before standardizing.

3·9 Preparation of Approximately 0.1 N Thiosulfate Solution. Heat one liter of distilled water (500 ml in each of two 600 ml beakers covered with watch glasses) to boiling, and continue to boil for five minutes to remove CO_2. While warm transfer to a clean one-liter glass-stoppered bottle. By means of a paper cone, add 25 grams of $Na_2S_2O_3 \cdot 5H_2O$ (weighed on triple beam balance) and 0.1 g Na_2CO_3 (a level microspatulaful). Shake thoroughly, and then store in the dark. The sodium carbonate is added to prevent disintegration of the thiosulfate ion.

3·10 Preparation of Starch Indicator. Stir approximately 2 g of "water soluble" starch in 20 ml of water (in a small beaker) to produce a paste. Slowly add the paste to 200 ml of boiling water, and continue to boil for two minutes. Cool, and store in a clean stoppered bottle.

The starch indicator should be freshly prepared before using since it is susceptible to bacterial action. However, even without the addition of preservatives, it is usually satisfactory for use over a period of about a week. Discard the suspension when it becomes definitely cloudy or when it gives a reddish color with iodine solution.

3·11 Standardization of Iodine Solution. Pure, primary-standard-grade arsenious oxide is to be found on the side shelf. Weigh out on the trip beam balance, on clean glazed paper, a portion of about 1.5 g, and place in a clean, dry weighing bottle. Dry in the oven at 110° C for at least one hour. Store in desiccator until needed.

Arsenious oxide is insoluble in water, and dissolves only slowly in acids. On the other hand, it is readily soluble in a high concentration of hydroxide ion as is indicated by the equation,

$$\underline{As_2O_3} + H_2O + 2\ OH^- = 2\ H_2AsO_3^-$$

The titration of the arsenite ion is not quantitative except in a buffered solution containing bicarbonate ions. In preparing the samples for titration it is essential that the directions in the next paragraph be followed in exact detail.

Weigh accurately (to 0.1 mg) three samples of arsenious oxide of about 0.2 g each, and transfer to 500 ml titration flasks. Add to each flask 10-15 ml of 1 N NaOH (prepare by adding 5 ml of 50% NaOH to 95 ml of water), and warm to hasten the solution of the arsenious oxide. Cool by immersing in cold water, add a piece of blue litmus, and then neutralize with 1 N HCl (prepare by diluting 8 ml of concentrated HCl to 100 ml with water) until the solution is distinctly acid. Add approximately 3 g of sodium bicarbonate to each flask. Dilute to about 100 ml, add 5 ml of starch indicator, and titrate to the first permanent appearance of a deep blue color.

CAUTION. The solution should not become acid during the titration. If the litmus paper turns red during the titration, add more $NaHCO_3$. Also, iodine tends to bleach litmus paper to a white color, and it may be necessary to add another piece of litmus paper. However, for best results, titrations should proceed at a pace such that bleaching is not permitted to occur.

The titration of the arsenite ion with iodine is not complete except in the presence of excess bicarbonate ions. The latter ions react with hydronium ions with the liberation of carbon dioxide. The two reactions are indicated in the following equations:

$$I_2 + H_2AsO_3^- + H_2O = 2\,I^- + H_2AsO_4^- + 2\,H^+$$

$$HCO_3^- + H^+ = H_2O + CO_2$$

Calculate the normality of the iodine solution. The average deviation should be less than 2 parts per thousand. The redox reaction involves the exchange of two electrons per arsenic atom; consequently, the milliequivalent weight of arsenious oxide which contains two arsenic atoms is 0.04945. This is obtained by dividing the formula-weight by 4000. The normality of the iodine is calculated from the formula,

$$\frac{\text{Weight of dried arsenious oxide in grams}}{\text{ml of iodine solution x 0.04945 g/meq}} = \text{N of iodine solution}$$

3·12 Standardization of Thiosulfate Solution. Several procedures have been developed for the standardization of thiosulfate against a number of primary standards, e.g., KIO_3, $K_2Cr_2O_7$, Cu, etc. However, it is not necessary to standardize both iodine and thiosulfate against primary standards. The normality of the thiosulfate can be determined satisfactorily by running a series of ratios against standard iodine solution. This is the same type of procedure as was performed in Sec. 2·6 in the acid-base exercise.

Procedure: Place the thiosulfate and iodine solutions in burettes following precautions given in earlier sections. Run out between 30-35 ml of thiosulfate into a titration flask, add 5 ml of starch solution, and dilute with 100 ml of distilled water. Titrate with standard iodine to the first permanent appearance of a deep blue color. Repeat until the average ratio of the two solutions is determined with a deviation of less than 2 parts per thousand.

Calculations: $\text{N of iodine} = \text{N of thiosulfate} \times \frac{\text{volume of thiosulfate}}{\text{volume of iodine}}$

3·13 The Iodimetric Determination of Antimony in Soluble Antimony. Antimony undergoes similar reactions with iodine to those described in Sec. 3·12. The principal difference is the fact that antimony tends to precipitate from dilute acid solutions in the form of insoluble SbOCl, as indicated by the equation,

$$Sb^{+++} + H_2O + Cl^- = \underline{SbOCl} + 2\,H^+$$

To avoid this possibility, tartaric acid is added to produce a stable, yet soluble, complex with antimony. The equation for the complex formation is usually written as,

$$SbCl_4^- + H_2C_4H_4O_6 + H_2O = H(SbO)C_4H_4O_6 + 4\,Cl^- + 3\,H^+$$

The potassium salt of this antimonyl tartrate complex is a soluble substance known as tartar emetic. It is available commercially and may be represented by the formula $KSbOC_4H_4O_6$.

Antimony in the form of an ore is somewhat difficult to get into solution; consequently, the analysis of stibnite--an ore of antimony--involves a painstaking procedure. On the other hand, commercially prepared samples of impure tartar emetic (the "soluble antimony" samples referred to in this section) can be analyzed without difficulty. They are fairly soluble in water, and since they already exist in the form of the tartrate complex, only a small amount of additional tartrate is necessary to prevent the possibility of precipitation through hydrolysis.

Procedure: Dry the sample containing soluble antimony at 110° C for at least one hour. After cooling, weigh accurately three portions on the analytical balance (between 0.7 and 1.0 g) to 0.1 mg. Transfer each portion to a 500 ml titration flask, and add 100 ml of distilled water. To the solution (or suspension) add approximately 2 g of potassium sodium tartrate, 3 g of sodium bicarbonate, and 5 ml of starch indicator; whirl until the mixture is uniform. Titrate with standard iodine to the first permanent appearance of a deep blue color. The titration reactions are usually designated as,

$$(SbO)C_4H_4O_6^- + I_2 + H_2O = (SbO_2)C_4H_4O_6^- + 2\,I^- + 2\,H^+$$

$$H^+ + HCO_3^- = CO_2 + H_2O$$

The redox reaction involves a change of two electrons per antimony atom; therefore, the milliequivalent weight of antimony is the atomic weight divided by 2000. Calculate the percentage of antimony in the sample, using the following formula:

$$\frac{\text{ml of iodine} \times N \times 0.06088\ \text{g/meq} \times 100}{\text{weight of sample in grams}} = \%\ \text{Sb in sample}$$

Results should agree within less than 3 parts per thousand.

3·14 The Iodometric Determination of Copper in Impure Copper Oxide. The number of substances that can be determined by iodometry is greater and more varied in nature than those by iodimetry. As was stated in Sec. 3·7, an iodometric analysis is an indirect iodine method in which an oxidizing agent liberates iodine from an iodide. Invariably the liberated iodine is titrated with thiosulfate solution, although solutions of arsenious acid or other reducing agents are possibilities.

The determination of copper is a typical, and widely used, example of the indirect iodine method. As in other analyses, it is more convenient to use impure copper oxide rather than a copper ore as the substance to be analyzed. It is generally true that the analysis of any ore involves a more complex procedure than that for an impure substance.

The cupric ion is an oxidizing agent which reacts with a soluble iodide according to the following equation:

$$2\ Cu^{++} + 4\ I^{-} = 2\ \underline{CuI} + I_2$$

Actually, the copper ion is a poor oxidizing agent, and the reaction is quantitative only because of the low solubility of cuprous iodide. Thus the reaction must be regarded as a precipitation process as well as an electron interchange. The liberated iodine is titrated, in the presence of the precipitated CuI, by standard thiosulfate solution.

$$I_2 + 2\ S_2O_3^{=} = 2\ I^{-} + S_4O_6^{=}$$

The two foregoing reactions are carried out in a highly buffered acetic acid solution since neither the iodine nor the thiosulfate solution is stable in strongly acid or basic solutions.

Experimental results indicate that cuprous iodide tends to adsorb iodine sufficiently to cause low analytical results. This difficulty is largely eliminated by the addition of the thiocyanate ion, which tends to displace adsorbed iodine on the CuI particles.

Procedure: Dry the impure sample at 110° C for at least one hour. Weigh out (to the nearest milligram) three samples between 1.5 and 2.0 g, into 500 ml titration flasks. Add 10 ml of 6 N nitric acid (conc. nitric acid is 15 N) and dissolve by warming gently. Dilute to 20 ml and add 5 ml of urea* solution (4 g in 100 ml). Boil for one minute and then cool in tap water. Dilute to 100 ml and add NH_3 until a deep blue color prevails. Boil to remove excess ammonia, then neutralize with acetic acid and add 3 ml in excess. Boil another minute, then cool to room temperature. Add 5 g of potassium iodide, dissolved in 10 ml of water, to each sample. Titrate with standard thiosulfate until the yellow-brown color of iodine is almost gone (but not quite). Add 5 ml of starch solution and continue titration, drop by drop, until deep blue color changes to gray. Add 2 grams of KCNS (or NH_4CNS) and swirl until the crystals are dissolved. Titrate just to the disappearance of the blue color, leaving a creamy white suspension of cuprous iodide.

Calculations: Since the redox reaction in the titration involves the interchange of only one electron, the milliequivalent weight of copper is the atomic weight divided by 1000, or 0.06354. The percentage of copper in the sample may be obtained from the following formula:

$$\frac{\text{ml of thiosulfate} \times N \times 0.06354\ \text{g/meq} \times 100}{\text{weight of sample}} = \%\ \text{of Cu}$$

The agreement among values should be within 3 parts in a thousand.

SUMMARY

The very large number of redox methods makes a fair sampling of such methods impossible. The four determinations included in this chapter are representative, but they do not provide a comprehensive overview of the many oxidation-reduction possibilities in quantitative analysis. Such a survey is beyond the limitations of time within a one-semester course. Outside readings pertaining to this area are recommended and urged for those students with inquiring minds. Your instructor will be glad to suggest references in this field.

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*The urea reacts with any oxides of nitrogen which may remain from the nitric acid treatment.

The calculations involved in redox methods of quantitative analysis depend on the relationship between electron charge and the equivalent weight. The student should note these relationships, emphasized in the experimental procedures.

Filtration techniques involving the use of a Gooch crucible and filter paper have been introduced. These techniques become increasingly important in later gravimetric determinations.

Chapter 4

COLORIMETRIC METHODS

PRINCIPLES OF SPECTROPHOTOMETRIC ANALYSIS

4.1 Terminology. When light passes through a transparent medium, the power of the light decreases because some light is absorbed. Colorless materials such as window glass absorb all wavelengths of visible light equally, thus the light is the same color coming out as going in. Other substances absorb certain wavelengths of light preferentially; the transmitted light, which is seen, and the absorbed light are of complementary colors. When white light is passed through $FeSCN^{++}$, green is absorbed and the transmitted light is red. Similarly, $CrO_4^{=}$ appears yellow, MnO_4^{-} purple, and $Cu(NH_3)_4^{++}$ deep blue, because the complementary colors are absorbed by these ions.

The quantitative amount of light absorbed, when light passes through a transparent medium, is dependent upon three variables:

$\underline{c}$, the concentration of the absorbing substance in the medium;

$\underline{b}$, the thickness, or length, of the medium; and

$\underline{a}$, the absorbancy index of the absorbing substance.

The absorbancy index is, in effect, a proportionality constant, whose value indicates how extensively each particle of the absorbing medium interacts with the wavelength of light being absorbed. To illustrate these three variables, respectively:

($\underline{c}$), light passes strongly through a dilute solution of $FeSCN^{++}$ (which is only weakly colored), but hardly at all through a concentrated solution;

($\underline{b}$), light passes easily through a thin layer of colored glass such as a sun shade, but thick stained glass windows keep the inside of a cathedral very dark;

($\underline{a}$), green light rays interact with and are absorbed much more strongly by red wine than by a white wine of similar concentration; similarly, yellow light is absorbed more strongly by a MnO_4^{-} solution than by a $CrO_4^{=}$ solution of equal concentration, causing the MnO_4^{-} solution to appear more opaque.

Quantitative measurements of the amount of light absorbed may be expressed in any of several ways; especially:

transmittance, T, the fraction of light transmitted ($\frac{\text{power out}}{\text{power in}} \equiv T$);

% transmittance, $\%T$, ($\frac{\text{power out}}{\text{power in}} \times 100 \equiv \%T$); and

absorbance, A, ($A \equiv -\log_{10} T = 2 - \log_{10} \%T = \log_{10} \frac{\text{power in}}{\text{power out}}$).

Of these, the absorbance is generally preferred for quantitative calculations and plots, because of the linear relationship between the logarithmic quantity designated by A, and the three factors a, b, and c; mathematically,

$$a \times b \times c = A = -\log_{10} T.$$

If the values of a and b are known, the concentration c can be determined by measuring the absorbance A. For a series of solutions having equal values for the product $a \times b$, the quantities A and c are directly proportional.

4·2 Methodology. Quantitative spectroscopy proceeds as follows. The problem: to analyze a solution which contains a certain known light-absorbing species in unknown concentration, C_x. The analyst prepares a series of solutions containing the same light-absorbing species, but in a variety of known concentrations, C_1, C_2, C_3,... He measures the absorbance of each of the solutions, while keeping variables a and b constant (by selecting a single wavelength of light for the analysis and using the same cuvette for each measurement). Then, plotting absorbance (vertically) against known concentration (horizontally), he obtains a linear graph, from which he can determine the concentration of the unknown by interpolation. This graphical method eliminates the necessity for knowing the exact values of a and b.

If the unknown solution happens to contain two light-absorbing components to be analyzed for simultaneously, then two wavelengths must be selected, two sets of known solutions must be measured, and two absorbance equations must be solved simultaneously for the two unknowns; etc. The accuracy of the method generally diminishes as the number of simultaneous unknowns increases, but it is significant that two unknowns often can be determined simultaneously by spectrophotometric measurements.

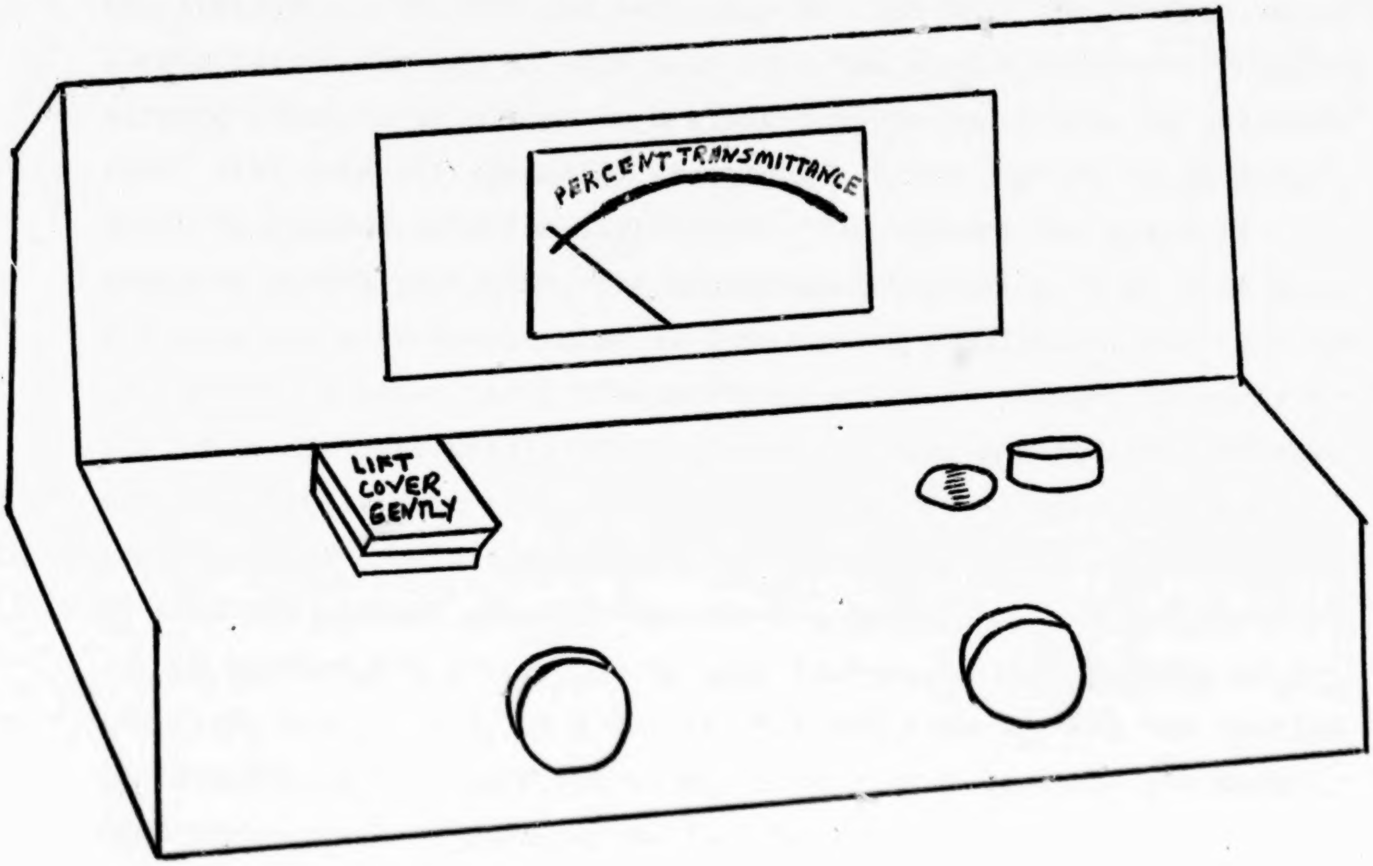

PERCENT TRANSMITTANCE
LIFT COVER GENTLY

Figure 4·1 The Bausch and Lomb "Spectronic 20" Spectrophotometer

4.3 Instrumentation. An instrument which can provide a particular wavelength of light and measure its transmittance through a solution is called a spectrophotometer. In the instrument, white light from a bulb is split up into its component wavelengths by a grating (or a prism); the grating can be oriented variously so that only the desired wavelength passes through an exit slit into the sample chamber. The absorbing solution is placed in a glass cuvette (much like an ordinary small test tube but specially constructed to be uniform in diameter) which is lowered into the light path. The transmitted light is measured with a phototube, the measurement appearing on a large meter. Although the absorbance value is more useful chemically, most spectrophotometers measure the % transmittance since it changes linearly with the power of light passing through the solution and thus can be read more accurately from the meter scale. From the %T readings, the corresponding A values are calculated using log tables, or else the %T data are plotted directly on semi-log paper.

A spectrophotometer also is used to measure the spectrum of a solution, i.e., the %T or A values of a solution for all the various wavelengths of the light spectrum. From such a spectrum the analyst determines the best wavelengths for the analysis.

Figure 4.1 provides a sketch of the Bausch and Lomb "Spectronic 20" Spectrophotometer which will be used in the experiment to follow.

ESSENTIAL TECHNIQUES IN SPECTROPHOTOMETRY

Several techniques, some of which are also common in general analytical work, are especially important in spectrophotometric analysis and are introduced in the present experiment.

4.4 Use of Volumetric Pipets. A pipet is a device which has been factory-calibrated to deliver (T.D.) a definite volume of liquid from one container to another.

Draw liquid up into the pipet by mouth suction or by squeeze bulb, until the meniscus falls well above the calibration mark on the upper stem. Quickly cap the pipet with the index finger (never the thumb). Tilt the pipet slightly and wipe the exterior free of adhering liquid.

To adjust the liquid level, hold the pipet in a vertical position over a waste beaker, and cautiously release the pressure upon the index finger so as to permit the meniscus (the bottom of the meniscus) to fall until it is exactly even with the calibration mark. Remove any hanging droplet of liquid by touching the tip to the side of the waste beaker. Finally, the liquid is allowed to drain freely from the pipet into the desired container (with the pipet almost vertical and its tip in contact with the glass wall), without forcing or blowing out the liquid remaining within the tip. This partial drop of liquid remaining in the pipet tip is accounted for in the factory-calibration of any T. D. pipet. If the pipet is properly clean, no droplets will remain clinging to the inner surfaces from which the liquid has been drained.

It is important to use mouth suction or squeeze bulb only to draw liquid into the pipet and not to adjust the level to the calibration mark. Some practice may be necessary before one becomes adept at removing the bulb with the free hand and quickly capping with the index finger of the hand holding the pipet; yet this is essential for good results.

Two additional precautions necessary in the proper use of the pipet are:

(1) In grasping the pipet, use only the thumb and first two fingers on the stem above the graduation mark. Never grasp the bulb of the pipet since it is calibrated at a definite temperature.

(2) As in the use of the buret, the liquid in the pipet must be completely free of air bubbles.

4.5 Use of Volumetric Flasks. A volumetric flask is calibrated to contain (T.C.) a specified volume of liquid at a specified temperature (generally 20° C). The bottom of the liquid meniscus should be made to coincide exactly with the calibration line on the flask neck. The flask has several different quantitative uses:

(1) Preparation of standard solutions. Analytical grade reagents may be weighed out carefully, dissolved, and diluted to the calibration mark to yield a solution of known molar concentration without need of further analysis. Thus, 1.824 millimoles of pure reagent diluted in a 10.00 ml

volumetric flask produces a solution that is 1.824 mmoles/10.00 ml, or 0.1824 M.

(2) Quantitative dilutions. Quantitative dilution is accomplished by pipetting a known volume of a solution into a volumetric flask, and diluting exactly to the new volume. Thus, a 15.00 ml pipetted sample can be diluted to 50.00 ml to yield a solution of molarity exactly 15/50 times as great as the original solution.

(3) Preparation of unknowns to known volume. Volumetric flasks are used also to dissolve samples of impure substances to a specified volume. From subsequent analysis of the molarity of the solutions and the known volume, it is possible to determine the number of moles of pure substance present in the impure sample.

4·6 Use of Cuvettes. Two matched cuvettes are used in the measurement of the %T of a solution. In the present experiment one will contain distilled water (pure solvent) and the other will be used for the various solutions of $Cu(NH_3)_4^{++}$ which you prepare. Matched cuvettes have similar size and curvature and show nearly identical effect upon a beam of light. The following RULES FOR HANDLING CUVETTES should be observed:

(1) Never touch the lower half of the cuvette, through which the light beam will pass.

(2) Lightly wipe off any liquid or smudges from the outer surfaces, using only the special wiping paper provided (absolutely nothing else will do!).

(3) Always rinse the cuvette with several small portions of solution before filling it for a measurement. (Only about 3 ml is needed for the measurement.)

(4) Notice the index line near the top of the cuvette. The cuvette should be placed in the spectrophotometer with the index line toward the front. After the cuvette is firmly seated, rotate the cuvette gently until the index line is aligned with that on the instrument. It is very important that the cuvette be aligned precisely the same way for each separate measurement.

(5) Dirty cuvettes should be rinsed several times with pure water and outside surfaces lightly wiped with wiping paper, after final use. Under

no circumstances may cleaning solution or test tube brushes be used on cuvettes.

4.7 Use of a Calibration Graph. A calibration graph is prepared from measurements of a series of solutions of known concentration. The measurement of a solution of unknown concentration is subsequently compared to the known measurements on the graph. In this type of graphical analysis, the accuracy of the calibration graph is of critical importance for obtaining accurate results. Known data must be plotted with care upon a grid of precision-ruled lines (a "home-made" graph or rough sketch is unacceptable).

In the present laboratory exercise the calibration graph should be a straight line (since Beer's Law is obeyed under the conditions of the experiment) which should pass through the origin of the graph (i.e., the point corresponding to zero absorbance vs. zero concentration, or 100%T vs. zero concentration). Any deviations of the measurements from a perfect straight line are indications of lack of precision, and repeat measurements should be made. Deviations may be due to faulty experimental technique (most likely), severe fluctuations in the A.C. line voltage (occasionally), and (to a small extent) inherent limitations imposed by the spectrophotometer itself. Occasionally, a point is simply misplotted.

The following are common technical errors in obtaining colorimetric data, which will subsequently yield inaccurate results:

(1) failure to keep the outer surface of the cuvette clean.
(2) failure to use the same cuvette for all measurements.
(3) failure to rinse the cuvette sufficiently with the new solution, before taking measurements.
(4) failure to orient the cuvette exactly the same way for each measurement.
(5) failure to account for slight "play" of the plastic cuvette holder within its cavity in the instrument.
(6) failure to set 0%T and 100%T carefully.
(7) inaccurate pipetting.
(8) inaccurate dilution within the volumetric flask.

(9) insufficient mixing of the solutions.

(10) use of unclean volumetric glassware.

The student is urged to take thoughtful care to avoid these many pitfalls in colorimetric analysis, and to notice any indication of such error when he plots the data graphically.

ANALYSIS OF COPPER IN COPPER OXIDE

4.8 Preliminary Observations. Special equipment provided for this experiment includes the following: a Bausch and Lomb "Spectronic 20" Spectrophotometer with constant voltage transformer, a cuvette rack containing two matched cuvettes and a third cuvette containing a piece of chalk with a diagonally-ground surface, a box of wiping paper, a marking pencil, a box of plastic wrap, and four Erlenmeyer flasks (250 ml or larger) with cork stoppers.

You will need from your desk also the following items: a 25-ml graduated cylinder, a 250-ml volumetric flask, a 25-ml volumetric pipet, two medicine droppers, a beaker for distilled water, and two 250-ml beakers for preparing the solutions.

You will need a sheet of linear coordinate graph paper and TWO sheets of semi-log graph paper (preferably one-cycle) supplied with the laboratory notes.

CAUTION: This entire experiment must be performed and completed on one day, the day it is assigned. Have the sample of copper oxide dried (110° C for one hour) and ready to weigh. Be thoroughly familiar with the procedures, so that you can use the limited time efficiently.

Plug in and turn on the spectrophotometer by rotating the left front knob clockwise. Use this knob to adjust the meter needle to 0%T. While the instrument is warming up (about 20 minutes), complete the following preliminaries and prepare the solutions as described below.

To observe what diffracted light passes through the sample cell, carefully insert the test tube containing the chalk into the sample holder. Make certain that the chalk's diagonal surface slopes downward toward the right. Rotate the 100%T-adjust dial (right front knob) clockwise; a band of color should appear upon the diagonal surface. Now rotate the wavelength dial (top right) and observe the variation in the color of the band, from violet and blue near 400 mμ to red near 700 mμ. (If you continue the rotation beyond 700 mμ to 1000 mμ, a repetition of the violet, blue, and green colors will be seen, due to second order diffraction from the grating. When the spectrophotometer is used at wavelengths greater than 700 mμ, a red filter must be inserted into the instrument so as to remove this second order diffraction light.)

Remove the tube with the chalk.

4.9 Preparation of Standard Copper Solutions. A stock solution of standardized cupric nitrate will be available in the laboratory. This stock solution is prepared by dissolving 4.000 g of 99.90% copper metal in nitric acid, and diluting quantitatively to exactly one liter of solution. Such a solution contains 4 mg of Cu per ml.

Obtain approximately 125 ml of the stock solution in a *clean*, *dry*, 250-ml beaker.

Using your 25-ml pipet, and the squeeze bulb, transfer exactly 25.00 ml of the stock solution from the beaker to your *clean* 250-ml *volumetric* flask (it need *not be* dry). Half-fill the volumetric flask with distilled water, so as to dilute the copper solution. In the hood, add small portions of concentrated ammonia (from a 25-ml graduated cylinder) with swirling, until a *clear* deep blue solution is obtained (after formation and redissolution of a milky-blue precipitate). Then add 30 ml concentrated ammonia in excess, and dilute to the mark with distilled water. Mix the solution well; store it in a clean, *dry*, 250-ml Erlenmeyer flask with cork stopper and appropriate labelling (solution I).

Repeat the above paragraph, so as to form a second known copper solution exactly like the first one (solution II).

Repeat the paragraph once again, this time pipetting *two* 25.00-ml portions of stock solution into the clean volumetric flask, so as to form a third known copper solution exactly twice as concentrated as the first two (solution III).

Prepare a "blank" solution (Solution 0) by diluting 30 ml of concentrated ammonia to 250 ml in a *clean* flask.

In your notebook prepare a table for the solutions you have prepared:

Concentration of Cu in the standard stock solution: ----mg/ml

Soln.	Ml. of stock soln. used	Final volume	Final concn. (calc'd.)
0	0.00	250.	----
I	25.00	250.0	----
II	25.00	250.0	----
III	50.00	250.0	----

4.10 Preparation of Unknown Solution from Copper Oxide. Weigh accurately one sample of dry copper oxide totalling about 2.5 g. Place the sample in an empty 250-ml beaker (clean). Add 30 ml of concentrated HNO_3 and 30 ml of distilled water, and warm gently in the hood to dissolve sample completely. Allow to cool. Again in the hood, add small portions of concentrated NH_3 from the 25-ml graduated cylinder with swirling until a clear deep blue solution is obtained (no cloudiness). Add 30 ml more NH_3, then transfer the solution quantitatively to an empty (clean) 250-ml volumetric flask, using distilled water for the rinsing. Finally dilute exactly to the 250-ml mark with distilled water. Mix the solution well.

Record the essential details regarding this "unknown" solution in your notebook.

4.11 Standardization of the Spectrophotometer.

(a) If necessary, rezero using the left front knob, with no cuvette in the instrument.

(b) Rotate the right front knob far counterclockwise.

(c) Rinse one of the cuvettes several times with the "blank" solution 0, fill half-full with the solution, dry the outside surfaces with wiping paper, cap with plastic wrap, and align the cuvette in the instrument as described above. Close the top of the sample holder.

(d) Rotate the right front knob clockwise, until the meter needle reaches exactly 100%T. (Do not allow the reading to exceed 100%T.) Now the spectrophotometer is standardized for the wavelength at which the instrument is set, for any sample containing dilute ammonia solution as the solvent.

Retain the cuvette, half-full, for later standardizations (henceforth called the "reference cuvette").

IMPORTANT:

The spectrophotometer must be standardized anew, by following the four steps outlined above, at EACH new wavelength setting before any quantitative measurements can be made upon solutions at that wavelength. This statement applies throughout the rest of the experiment.

4.12 Measurement of the Visible Spectrum of $Cu(NH_3)_4^{++}$. The spectrum is measured in order to determine the best wavelength to use for the analysis of the unknown solution.

Set the wavelength at 450 mμ (right upper dial) and standardize as above. Remove the reference cuvette. Half-fill the other cuvette (the "sample cuvette") with your Solution III, after pre-rinsing with the solution. Wipe the cuvette dry, cap with plastic wrap, and align in the instrument. Record the %T reading at this wavelength. Readjust "0" and "100" as before, and remeasure the %T of the sample solution, until you are satisfied with the average %T reading obtained.

Continue this procedure at each of these new wavelength settings: 475, 500, 525, 550, 575, 600, 625, 650, and 675 mμ. Record in a table:

Wavelength (mμ)	%T reading	What solution measured?
450	...	...

After obtaining the data, plot them on semi-log paper, with %T plotted on the logarithmic scale. Connect the data points (each circled) with a smooth curve. On the graph, denote with a bracket, $\underbrace{\qquad}$, a relatively flat region of the $Cu(NH_3)_4^{++}$ spectrum where the solution absorbs light strongly. Such a region is most apt to be desirable for quantitative analysis.

4.13 Analysis by Beer's Law Plot. The absorption of each prepared solution is measured at the chosen wavelength. The method of analysis has been discussed in Section 4.2.

(a) Empty and rinse thoroughly the "sample cuvette", and fill it with Solution O.

Set the spectrophotometer to wavelength 600 mμ.

Restandardize the instrument using the "reference cuvette"; then measure %T of the "sample cuvette" containing Solution O -- 0.00000 mg Cu^{++}/ml. Repeat several times, and record in a table each %T measurement.

Solution	Concentration (mg Cu/ml)	%T measured	%T average	A, calculated	Wavelength (mμ)
0	0.00000	---			
		---	---	---	600

		(should be 100%)		(should be zero)	

Rinse the sample cuvette repeatedly with Solution I. Then measure several times the %T of the Solution I at 600 mμ. It is desirable to restandardize the instrument for each measurement.

Similarly, measure the %T of Solutions II and III and the unknown solution, each time with appropriate rinsing of the cuvette.

(b) Plot %T vs. mg/ml concentration on semi-log graph paper -- a Beer's Law plot. If all the measurements made with the known solutions do not fall on a straight line, recheck your values and calculations and consult your instructor. Always enclose each data point within a small circle.

After constructing the Beer's Law plot, locate on it the measurement made with the unknown sample solution, and thereby determine the concentration of the unknown solution (in mg/ml). Enclose this measurement in a square box, to distinguish it from the other measurements used to prepare the graph.

Calculate the %Cu in the copper ore sample. The mathematical relationship is:

$$\%\text{Cu} = \frac{(\ldots\text{mg/ml Cu in vol. flask}) \times (250.00\text{ ml}) \times 100}{(\ldots\text{g Cu unknown sample placed in flask}) \times (1000\text{ mg/g})}$$

(c) When you have finished, empty and thoroughly rinse the cuvettes with water. Return to your desk any equipment which belongs to you. Neatly arrange the items which were provided as special equipment for the experiment. Leave the workspace in clean condition. Unplug the spectrophotometer.

(d) Submit the following as a special laboratory report within one week after you complete the laboratory work.

(1) the semi-log plot of the spectrum of the ammoniacal Cu^{++} solution, prepared in Sec. 4.12.

(2) the semi-log plot of %T vs. concentration, prepared in Sec. 4·13.

(3) the %Cu in the solid unknown, as calculated in Sec. 4·13, plus an estimate of the probable uncertainty in your answer (i.e., ± ... %). Explain your reasoning briefly but clearly.

(4) a graph of A (calculated from the %T data using a logarithm table) vs. concentration, plotted on ordinary graph paper -- concentration on the horizontal axis. Use the data for the known solutions to determine the straight line, and determine the concentration of the unknown, in the manner of the semi-log plot.

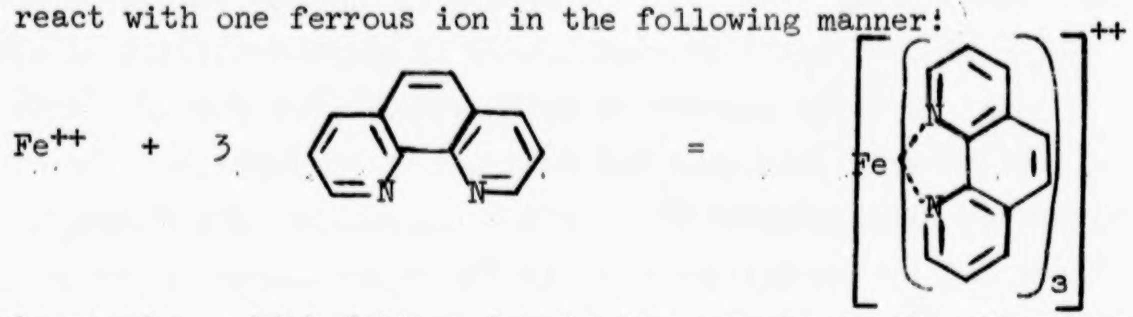
All graphs should be labelled with full details regarding the chemical systems under study, the nature of the data plotted, and the date of measurement, so that each graph is self-sufficient.

4·14 Critical Comments. Several diverse methods of analysis are available for analyzing solutions containing copper ion in bulk, such as the excellent electrogravimetric analysis where the copper is plated out quantitatively on platinum electrodes by forced flow of electrical current. The foregoing spectrophotometric analysis in aqueous ammonia medium gives less precise results, but was chosen for this course for two principal reasons: it is a comparatively simple procedure involving readily available chemical substances, yet it provides some first-hand experience with the very important technique of colorimetric analysis and use of a spectrophotometer.

Colorimetric methods for copper analysis are used most often for determination of trace amounts of copper. A wide variety of organic, complexing reagents form distinctive copper complexes with high absorbancy indexes and high light-absorbing properties. To improve further the precision, a technique (known as precision colorimetry) is employed. The experimental procedure is modified by setting the 100%T reading on the meter by use of a dilute solution of known copper concentration rather than with pure water, so as to increase the precision with which the unknown solution can be measured. Additional electronic circuitry may be used to maintain more constant voltage. Possible impurities may be controlled more rigorously in the unknown solutions. Due to limited laboratory time, such more accurate procedures are excluded from the present course.

COLORIMETRIC DETERMINATION OF FERROUS IRON

4.15 Preliminary Comments. One of the most sensitive methods for the determination of iron is based upon the formation of the orange-red ferrous-orthophenanthroline complex ion. Three molecules of 1,10-phenanthroline react with one ferrous ion in the following manner:



The chelate complex, which follows Beer's Law closely in its absorbance, is very stable and remains unchanged over a long period of time.

Orthophenanthroline is a weak base, behaving similarly to ammonia, in reacting slightly in water solution to give the phenanthrolinium ion and hydroxide ion,

$$\text{phen} + \text{HOH} = \text{phen H}^+ + \text{OH}^-$$

In an acid solution the principal species present is the phenanthrolinium ion (analogous to the NH_4^+ ion); consequently, the complex formation in acidic solution may be indicated by the following equation:

$$\text{Fe}^{++} + 3\ \text{phen H}^+ = \text{Fe(phen)}_3^{++} + 3\ \text{H}^+$$

The equilibrium constant for the reaction is 2.5×10^6, which strongly favors complex formation. However, the position of the equilibrium is somewhat dependent upon pH. If the pH is below 2, the reaction is incomplete, resulting in a weak color. Usually a pH of about 3.5 is recommended for the analysis, although the color is stable within a pH range of 2-9, and a more careful control of this variable is not necessary.

Ferric iron is reduced by adding an excess of hydroquinone. The ferrous iron remains stable as the ferrous-orthophenanthroline ion for many months.

4·16 Reagents. The reagents for analysis are usually prepared by the instructor, and are available in the laboratory. For informational purposes, the preparations are indicated as follows:

Hydroquinone solution. A one per cent solution is prepared by shaking the compound in distilled water, and buffering it with sodium citrate to an approximate pH of 4.5.

Sodium citrate solution. 250 grams of the dihydrate is added to sufficient distilled water to make one liter of solution.

1,10-Phenanthroline solution. 0.5 per cent solution of the monohydrate in distilled water is used. Warm to effect solution and store in dark; discard the solution when it becomes colored. Two milliliters of this solution is required for each milligram of iron.

Standard Iron Solution. 0.3511 g of reagent grade ferrous ammonium sulfate is dissolved in 100 ml of distilled water; add 1 ml of concentrated sulfuric acid, and dilute exactly to one liter in a volumetric flask. One milliliter of the standard iron solution contains 0.05 mg of iron.

pH Paper, to cover the approximate range of 3.0 to 5.0, such as pHydrin paper.

4·17 Procedure. Review Secs. 4·1 - 4·8; the Use of Cuvettes is of special importance. The special equipment provided for this experiment is the same as that detailed in Sec. 4·8.

Preparation of Diluted Standard Iron Solutions. Obtain approximately 150 ml of standard iron solution (containing about 0.05 mg Fe/ml) in a clean, dry, 250-ml beaker. The exact concentration of Fe is indicated on the bottle label.

Using your 25-ml pipette, transfer 25.00 ml of the stock solution from the beaker to your clean 250-ml volumetric flask (it need not be dry). Half-fill the volumetric flask, so as to dilute the iron solution. Add sodium citrate solution dropwise to the flask. Shake the flask after each addition (only a few drops will be necessary). The flask should be stoppered with a leak-proof plastic stopper. Touch the damp stopper against a piece of pH paper. Continue to add sodium citrate dropwise until pH paper indicates a pH between 3.0-4.5. (Avoid excessive testing with the pH paper, so as to avoid undue loss of solution.) With a graduate, add 8 ml of hydroquinone solution and 8 ml of orthophenanthroline solution. Dilute to mark with distilled water. Mix the solution thoroughly, then transfer for storage to a clean, dry, 250-ml Erlenmeyer flask, fitted with a cork stopper and labelled Solution I.

Repeat the instructions given in the previous paragraph, this time pipetting two 25.00 ml portions of the standard iron solution into the clean 250-ml volumetric flask, so as to produce a second known iron solution which is exactly twice as concentrated as the first one. Label the 250-ml Erlenmeyer flask used for storage as Solution II.

Repeat the instructions once again, this time pipetting three 25.00 ml portions of the standard iron solution into the clean 250-ml volumetric flask, so as to obtain a third known iron solution which is exactly three times as concentrated in respect to iron as is the first solution. Label the Erlenmeyer flask in which this solution is stored as Solution III.

Prepare a "blank" solution, designated as Solution 0, by diluting 8 ml of hydroquinone and 8 ml of orthophenanthroline to approximately 250 ml in a clean Erlenmeyer flask. No adjustment of pH is necessary.

In the notebook prepare a table for the solutions that have been diluted, calculated on the basis of the known concentration (---- mg Fe/ml) of the original standard iron solution.

Diluted Standard Iron Solutions

Solution	Ml of Standard solution used	Final Volume	Final concentration, mg Fe/ml (calc'd.)
0	0.00	250.	0.0000
I	25.00	250.0	
II	50.00	250.0	
III	75.00	250.0	

Preparation of Unknown Solution of Impure Ferrous Ammonium Sulfate. Obtain an unknown sample from instructor. This material is not to be dried, because at elevated temperatures the sample would lose water of hydration (part of its original composition) in a non-quantitative fashion, and the iron would be slowly oxidized (resulting in further change in composition).

Weigh out (to 1 mg) approximately one gram into a 400 ml beaker. Add 100 ml of distilled water and 1 ml of concentrated H_2SO_4. Stir thoroughly until solution is effected; then transfer quantitatively to a one liter volumetric flask, and dilute to mark. Mix thoroughly for not less than 20 minutes by repeatedly inverting the flask (fitted with a plastic leak-proof stopper).

Using the 25-ml pipette, transfer 25,00 ml of the unknown solution to a clean 250-ml volumetric flask (it need not be dry). Half-fill the volumetric flask with distilled water; add sodium citrate dropwise, and test for pH as described in Preparation of Diluted Standard Solution in this section. When the pH is between 3.0-4.5, add 8 ml of hydroquinone solution and 8 ml of orthophenanthroline solution, and dilute to mark with distilled water. Mix the solution thoroughly; this is your prepared Unknown Solution.

4·18 Operating Instructions for the Spectronic Colorimeter. Detailed instructions for the operations of the "Spectronic 20" colorimeter are given in Secs. 4.11 and 4·12. These instructions still apply, but will not be reiterated in toto. Condensed directions are as follows:

Turn on the instrument with left front knob and allow to warm up for about 20 minutes. Since the absorbancy spectrum exercise is given in Sec. 4·12, for the $Cu(NH_3)_4^{++}$ complex, it is not necessary to repeat this exercise for the ferrous-orthophenanthroline complex. It has been determined, experimentally, that the wavelength of maximum absorbance for the ferrous complex is 508 mμ. Set the wavelength dial (top, right-hand knob) at 508. With sample compartment empty, adjust the left-front knob so that the meter pointer reads zero per cent transmittance. Insert Solution 0, and adjust the right-front knob so that the meter pointer reads 100% transmittance. Replace the Solution 0 with Solutions I, II, and III, and with the unknown solution. Use the same cuvette for all measurements, rinsing it well with each solution before testing. Determine duplicate or triplicate %T measurements on separate portions of each solution. From the data of the four standards (Solutions 0, I, II, III) prepare a calibration curve, which should be a straight line on semi-log paper, in terms of (log)%T versus mg Fe/ml in the samples.

From the %T data of the unknown, ascertain the mg of Fe/ml in the unknown; then calculate the per cent of Fe present. Record all data.

When you have completed this exercise, empty and thoroughly rinse the cuvettes with water. Return to your desk any equipment which belongs to you. Neatly arrange the items which are provided as special equipment for the experiment. Leave work space in an orderly condition. Unplug the spectrophotometer.

4.19 Calculations. For clarification, part of the previous instructions are repeated: Plot per cent transmittance versus mg of Fe/ml on semi-log graph paper. If a straight line is obtained, it verifies Beer's Law. If all the measurements do not fall on a straight line, recheck your values and calculations, and consult with your instructor. Always enclose each data point within a small circle; indicate the concentration of the unknown solution in a square box to distinguish it from the other measurements used in preparing the graph.

The mathematical relationship in calculating the percentage Fe in the sample of ferrous ammonium sulfate is as follows:

$$\frac{\text{---- mg Fe/ml} \times \text{dilutions } (1000 \times 10) \times 100}{\text{Wt. of unknown sample} \times 1000 \text{ mg/g}} = \%\ \text{Fe}$$

Chapter 5

PRECIPITATION METHODS

VOLUMETRIC METHODS

5·1 Preliminary Comments. Volumetric methods of analyses which make use of precipitate formations are usually designated as precipitation titrations. In order to be usable volumetrically, a precipitate must form rapidly and be fairly insoluble. In other words, the reaction should be complete at the equivalence point if possible. Moreover, an indicator must be available that will produce an observable change in the solution (or precipitate) near the equivalence point. Because of these limitations, relatively few precipitation reactions are satisfactory for precipitation titrations.

The most widely used precipitate-formation titrations are those involving the silver ion versus the various halides and pseudo-halides. These procedures are frequently called argentometric precipitation methods. As typical examples of these methods, the Mohr method for the chloride and the adsorption indicator method for the same ion have been selected for laboratory exercises. Alternately, an emf graphical method is used, involving a pH meter as detector with a silver wire as the indicator electrode (see Secs. 5·5 and 5·6).

5·2 Preparation of Approximately 0.1 M Silver Nitrate. Normality, molarity, and formality are the units most frequently used in designating concentrations of solutions. The term formality is probably the most unambiguous expression for the concentration of an ionic compound; however, the use of molarity as a concentration unit has become so deeply entrenched in the chemical literature that it seems unwise to substitute even a better term. By definition, a molar solution contains one gram molecular weight (usually abbreviated to one mole) of a solute dissolved in sufficient water to make a liter of solution. Thus, a 0.1 M solution of silver nitrate contains one-tenth of a mole of this salt in a liter of solution.

Procedure. Counterpoise a clean, dry 50-ml beaker on a triple beam balance and weigh into it 17 g of pure, dry $AgNO_3$ (as furnished--do not dry in oven). Proceed to the analytical balance and weigh beaker plus silver nitrate to 0.001 g; record the weighing on a right-hand page of the notebook. Carefully, avoiding any loss, transfer as much as possible of the crystalline $AgNO_3$ into a clean, but not necessarily dry, 250-ml beaker. Reweigh the original 50-ml beaker to 0.001 g, record, and take the difference from the first weighing as the actual weight of the $AgNO_3$.

Working quantitatively, dissolve the $AgNO_3$ (now contained in the 250-ml beaker) in approximately 75 ml of water; then transfer the solution without loss to a clean one-liter volumetric flask. The procedure for quantitative transfer of the solution is illustrated in Fig. 5·1. Place a clean analytical funnel in the flask. Hold a stirring rod vertically above the funnel and pour the solution from the beaker down the rod, keeping the spout of the beaker against the rod. After all of the solution is out, rinse beaker and rod, as illustrated, with distilled water. Make certain that the stream of water reaches all of the inside surface of the beaker. After rinsing, remove the beaker and rod; withdraw the funnel slowly while rinsing both the inside and outside of the stem. Now direct a stream of water down into the volumetric flask to remove any solution which may have adhered near its mouth.

Next pour distilled water, from a clean beaker, into the volumetric flask until the solution level is just below the graduation mark on the stem of the flask. Allow solution to reach room temperature, then add distilled water drop by drop from a pipette until the liquid level meniscus coincides with the graduation mark. Mix thoroughly by inverting flask back and forth for at least five minutes. (The flask should be stoppered with a leak-proof plastic stopper.) Do not use the neck of the flask as a handle.

Calculation: From the known weight of $AgNO_3$ contained in the one liter (exactly measured) of solution thus prepared, calculate, and record in notebook, the molarity of the solution.

$$\text{Molarity} = \frac{\text{weight of the } AgNO_3 \text{ in grams}}{\text{ml of solution} \times \text{millimolecular weight of } AgNO_3}$$

For example, if you weighed out 17.130 grams of $AgNO_3$ and dissolved it in exactly one liter of solution, then,

$$\text{Molarity} = \frac{17.130 \text{ grams}}{1000 \text{ ml} \times 0.1699 \text{ g/mmole}} = 0.1008 \frac{\text{mmole}}{\text{ml}} \text{ or M}$$

This is a hypothetical example, your molarity will be different.

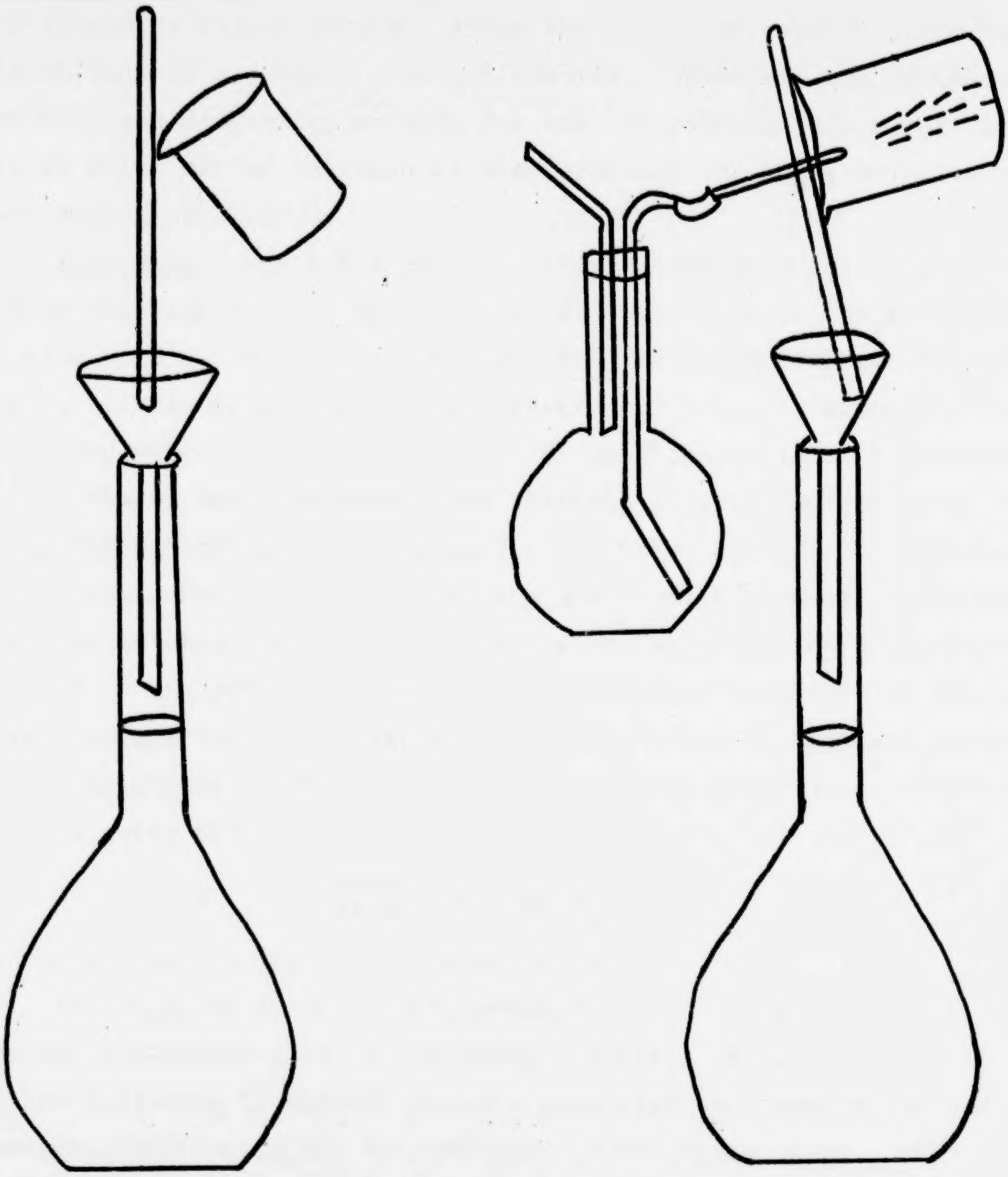


Figure 5·1 Quantitative transfer of solution to volumetric flask.

5·3 Standardization of Silver Nitrate Solution by the Mohr and Adsorption Methods. The molarity for the $AgNO_3$ solution obtained in Sec. 5·2 should be fairly accurate since the purity of reagent grade $AgNO_3$ is almost that of a primary standard chemical. However, the procedures for the Mohr and adsorption methods for the chloride contain slight inherent errors which may be canceled by standardizing the $AgNO_3$ solution against pure sodium chloride.

Procedure. Dry a 2 g portion (triple beam balance) of primary-standard sodium chloride for one hour at 110° C. Weigh out on the analytical balance to 1 mg, a sample of the dry NaCl of 1.4 to 1.5 g. Transfer quantitatively to a clean 150-ml beaker. Dissolve in about 60 ml of distilled water, transfer the solution quantitatively to a 250-ml volumetric flask, wash the beaker and stirring rod, and add washings to the flask taking care not to fill above the mark. (Follow the techniques described in Sec. 5·2 concerning the quantitative transfer of a solution.) When the solution has reached room temperature fill the volumetric flask exactly to the graduation mark. Mix thoroughly by inverting the volumetric flask (stoppered with a leak-proof plastic stopper) back and forth for about ten minutes. The molarity of the sodium chloride is obtained from the following formula:

$$M = \frac{\text{weight of NaCl in grams}}{250 \text{ ml} \times 0.05844 \text{ g/mmole}}$$

Record the NaCl molarity in the notebook.

The chloride solution just prepared is to be used in Parts I and II for the standardization of the $AgNO_3$ solution. Note carefully that both of the following titrations require good light to observe the end points; however, they should not be performed in direct sunlight. (Even in artificial light the precipitate will darken if the titrations are performed too slowly.) Conserve the NaCl solution as much as possible in order that it may suffice for 6 to 8 titrations, each involving 25 to 30 ml.

Part I. Standardization by Adsorption Indicator Method. Using the least quantities of reagents necessary for rinsing, fill one burette with $AgNO_3$ solution and the other with the NaCl solution. Read and record both burettes. Run into a clean 500-ml titration flask about 25 ml of the chloride solution and add approximately 25 ml of distilled water. Stir in 6-8 drops of dichlorofluorescein indicator and 0.1 g of dextrin (a level microspatulaful, no more). The dextrin stabilizes the colloidal state of the precipitate.

Titrate fairly rapidly with $AgNO_3$ solution; inasmuch as slow titrations may permit the precipitate to darken and thereby obscure the end point. At the end point there is a sudden change from white to pink in the color of the AgCl particles*. It is necessary to whirl the solution constantly; otherwise, there is a tendency for the AgCl particles, which indicate the pink end point, to settle to the bottom of the flask. Since the end point is somewhat reversible, it is sometimes possible to run back and forth across the point at which the pink and white particles are differentiated. This is accomplished by adding alternately a slight excess of $AgNO_3$ or NaCl solution. Having determined duplicate titrations, calculate at once in order to ascertain whether it is necessary to make additional titrations, to secure a precision of 2 parts in a thousand. Assume that the NaCl molarity is more accurate than the $AgNO_3$ molarity. The molarity of the $AgNO_3$ may be obtained from the following formula:

$$\underset{(AgNO_3\ \text{solution})}{\text{ml} \times \text{M}} = \underset{(\text{NaCl solution})}{\text{ml} \times \text{M}}$$

Record the $AgNO_3$ molarity in the notebook, designating it as obtained by the adsorption method.

---

*The color change of the AgCl particles occurs when negatively charged, colored dichlorofluorescein ions become adsorbed on a positively charged colloidal surface. This change occurs at the equivalence point because the electrostatic charge on the surface of the colloidal AgCl particles goes then from negative (in presence of excess untitrated chloride) to positive (in presence of excess silver ions).

Part II. *Standardization by the Mohr Method*. After the burettes have been filled (as directed in Part I) with $AgNO_3$ and NaCl solutions, respectively, and the readings recorded, measure approximately 25 ml of the NaCl solution into a medium-size porcelain casserole (300 ml or larger). A flask or beaker does not permit a good observation of the end point. Add 25 ml of distilled water (graduate) and 2 ml (graduate, or 40 drops) of 0.1 M K_2CrO_4 indicator solution. Without further dilution titrate fairly rapidly with the $AgNO_3$ solution to the first permanent change in tint from lemon yellow to orange.* During the titration stir the solution constantly with a short stirring rod. Before taking the burette readings, run back and forth across the end point by the alternate additions of a few drops of excess $AgNO_3$ and NaCl solutions. Make at least three independent titrations. From the average of concordant results, calculate and record the *molarity* of the $AgNO_3$ as obtained by the Mohr method. The calculations are similar to that indicated for the adsorption method as given in Part I.

For your convenience and that of your instructor you should record, in tabular form, the *molarity* of the silver nitrate solution as determined by each of the three methods of standardization. A suggested form, for your notebook, is given as follows:

Consolidated Record of Standardization of Silver Nitrate Solution

Molarity

A. From method of preparation (direct weighing of silver nitrate crystals)........................... ________

B. From NaCl standardization with adsorption indicator (average)................................ ________

C. From NaCl standardization by the Mohr method (average).. ________

---

*The color change from lemon yellow to orange occurs when the dissolved $CrO_4^{=}$ ions (lemon yellow) first begin to be precipitated by excess Ag^+ titrant (as red Ag_2CrO_4 precipitate), indicating that the chloride ions present in the sample have already been precipitated (as less soluble, white AgCl).

5·4 Analysis of Unknown Chloride Sample by Adsorption and Mohr Methods.

Dry the sample of unknown chloride for at least one hour at 110° C. Weigh out on the analytical balance, to 1 mg, about 5 grams of the material and record weight in notebook. Transfer the weighed portion to a clean, dry 150-ml beaker.

Working *quantitatively*, as described in Sec. 5·2, dissolve the weighed portion in about 60 ml of distilled water, and transfer the resulting solution to a 250-ml volumetric flask. (The flask should have been cleaned thoroughly with distilled water after its use in Sec. 5·3.) Follow procedure given in Sec. 5·2 in filling flask to graduated mark. Mix thoroughly for at least 10 minutes.

Analysis by the Adsorption Method. Fill the burettes, respectively, with standard $AgNO_3$ solution and the solution of unknown chloride, taking care to waste as little as possible of the latter solution. Using the procedure of the Adsorption Indicator Method as described in Sec. 5·3 (Part I), complete three or four titrations. In each titration use about 20 ml of the chloride solution. From the molarity of the $AgNO_3$ solution, as obtained by the adsorption method (Sec. 5·3-Part I), calculate and record the percentage of chloride in the sample. The formula for the calculation is as follows:

$$\frac{\text{ml of AgNO}_3 \times \text{M of AgNO}_3 \times 0.03545\ \text{g/mmole} \times 100}{\text{weight of sample in grams} \times \dfrac{\text{ml of unknown chloride}}{250\ \text{ml}}} = \%\ \text{Cl}$$

In the formula, the product "ml of $AgNO_3$ x N of $AgNO_3$" is the number of millimoles of $AgNO_3$ used as titrant, which is equal numerically to the number of millimoles of chloride ion precipitated. To convert from *millimoles* of chloride to units of mass (*grams*), the conversion factor 0.03545 g/millimole is used. Thus the formula compares the mass of chloride ion precipitated (numerator) with the mass of sample originally present in the particular volume of unknown solution used for the titration (denominator).

Analysis by the Mohr Method. Complete three or more titrations with about 20 ml of the unknown solution, using the technique of the Mohr Method as practiced in Sec. 5·3 (Part II). Calculate the percentage of chloride in the sample by the same formula as in the foregoing paragraph, but, in the present calculation, use the molarity of the $AgNO_3$ which was obtained by the Mohr Method (Sec. 5·3-Part II).

Consolidated Report on the Analysis of Unknown Chloride. The procedures in arriving at the final percentage of the unknown chloride are somewhat lengthy; consequently, a simple report on the analyses will suffice. Make the report as follows:

Exp. 5·2-5·4 Precipitation Titration of Unknown Chloride Name

Average of Adsorption Method __________

Average of Mohr Method __________

If your results are inaccurate, your instructor will want to examine the records pertaining to the analyses. These records should be complete and arranged in an orderly fashion.

POTENTIOMETRIC PRECIPITATION TITRATION

5·5 Preliminary Comments. Potentiometry involves measurements of the difference in potential (electromotive force) between the two electrodes of a galvanic cell. A series of potentiometric measurements are obtained at various times during the course of a titration, the repeated small additions of titrant causing changes in the composition of the solution in the cell and coincident changes in the measured potential. By plotting the potential vs. ml of titrant, the measurements yield a curved line which reveals information about the composition of the original solution -- as well as data useful for calculation of equilibrium constants such as K_{sp}.

pH titration (see Sec. 2·8) is a special type of potentiometric titration, in which the instrument yields readings directly in units of pH, because of appropriate arrangement of internal electronic circuitry within the instrument and use of a buffer solution for calibration. In ordinary potentiometric titration, the readings are in volts (or millivolts).

As in pH titration, the two electrodes of the galvanic cell are given distinctive names to tell their respective functions (see Sec. 2·9). The indicator electrode has a potential which is dependent upon the concentration of the substance being titrated. The reference electrode maintains a constant potential with respect to the solution, regardless of any change in the concentration of the ions in the solution. Since it is the difference in potential between the two electrodes which is measured, any change in potential as a result of titration is evidence of a similar change in the indicator electrode's potential. The galvanic cell as a whole may be represented as,

Indicator electrode $||$ Reference electrode
(emf changes during titration) (emf remains constant during titratic

The parallel vertical lines refer to a salt bridge or similar form of electrolytic contact needed between the two electrodes.

Potentiometric methods can be applied to many precipitation titrations, the main limitation being availability of suitable indicator electrodes. In theory, any metal, when bathed by a solution of its ions, should serve this purpose; but in practice, only a few electrodes are satisfactory. (Many metals tend to form insensitive oxide coatings which render the electrode either irreversible or inert.) The silver electrode is one of the most widely used of the indicator electrodes, partly because silver has little tendency to form an oxide coating, and partly because of the large number of insoluble salts formed by silver ion.

The best known precipitation titration with the silver electrode is the determination of the halides, i. e., the titration of chloride, bromide, and iodide ions with silver nitrate. The potential of the silver electrode is a logarithmic function of the concentration of the silver ions remaining unprecipitated in solution.

$$E_{Ag^+/Ag} = E^o_{Ag^+/Ag} + \frac{2.3\ RT}{n\mathcal{F}} \log[Ag^+]$$

When, during a titration, a rapid change occurs in the logarithm of the Ag^+ concentration, there is also a rapid change in the potential measured. Detection of the rapid change provides information about the composition of the solution.

Consider the titration of a chloride solution with silver nitrate titrant, as a convenient example.

Early in the titration most of the added silver ions will be precipitated as silver chloride. The high concentration of excess chloride ion keeps the silver ion concentration at a low value according to the K_{sp} relationship for silver chloride: $K_{sp} = [Ag+][Cl^-]$

During the early portion of the titration, only small changes occur in the logarithm of the silver ion concentration, and the potential changes only slightly.

Near the equivalence point the concentration of excess chloride ion rapidly decreases and the concentration of silver ion rapidly increases by several powers of ten. Large changes occur in the logarithm of the concentration, and in the potential measured.

Well beyond the equivalence point the concentration of silver ion is large, because there is now a continual excess of silver ion present in the solution; so again only small changes occur in the logarithm of the concentration. The equivalence point occurs when the concentration of silver ion and chloride ion are equal.

$$K_{sp} = [Ag^+][Cl^-]$$

At the equivalence point, $[Ag^+] = [Cl^-] = K_{sp} = \sqrt{1 \times 10^{-10}} = 1 \times 10^{-5}$ M

A typical potentiometric curve is sketched in Figure 5·2. Notice the appreciable change in potential in the vicinity of the equivalence point. It is necessary to obtain numerous potentiometric readings in this region (i.e., very small and equal increments of titrant should be added) so as to be able to locate the equivalence point accurately (the midpoint of the steep rise in the curve). The arms of the curve, extending more nearly horizontally, may be determined with only three or four readings each. Therefore, large increments of titrant are sufficient in the regions preceding and following the vicinity of the equivalence point. In general, the desired number of data and relative spacing, for which one should strive, is comparable to that for pH titration measurements (Sec. 2·9).

In Sec. 5·6 a procedure is given for the titration of an unknown chloride solution with standard silver nitrate solution. A pH meter which permits millivolts to be read from the scale serves as a convenient potentiometer for the titration. The indicator electrode may be either a piece of pure silver wire, a silver "billet", or a platinum wire or gauze plated with silver. As reference electrode a calomel electrode, or, more conveniently, a glass electrode may be used, since no significant change in pH occurs during the titration. Use of a side-arm type of calomel electrode requires the presence of a potassium nitrate salt bridge, because the usual potassium chloride salt bridge will contaminate the titration solution with extraneous chloride ions. A calomel electrode with a fiber junction is acceptable, since diffusion of chloride ion through the fiber into the titration solution is negligible, but there is likelihood of clogging of the fiber with fine crystals of silver chloride, disrupting the electrolytic contact and producing unsteady meter readings.

Precipitation titrations require up to five minutes of rapid mechanical stirring before equilibrium is attained, especially near the equivalence point. The approach to equilibrium is indicated when the measured emf does not drift more than 3 or 4 millivolts. The titration must be continued well beyond the equivalence point in order that a graph of the measurements will produce a symmetrical curve.

Many graphical methods have been devised for analyzing data from a potentiometric titration -- for example, plotting first or second derivatives of the potential change as the titration proceeds. With manual measurements, none of these methods has any particular advantage over a simple graph of potential (mv) vs. volume of titrant added (ml). The methods are useful primarily in automated detection systems where, for example, the derivatives of the potential change are determined electronically and the results plotted by servo recording devices. For routine work automation permits more efficient and rapid analyses with less use of manpower, but does so at the expense of accuracy.

5·6 Procedures. The instructor will assign a pH meter to you for use as a potentiometer in the experiment. Refer to the instruction pages and the diagram for that pH meter, for directions as to the proper operating procedure (see Appendix). Operate the instrument on the 1400 millivolt setting for EMF measurement. As indicator electrode, use a simple silver wire (attached to the instrument by a special connector provided -- see Fig. 5·3) or a commercial silver metal electrode; plug the electrode into the reference terminal at the rear of the instrument. As reference

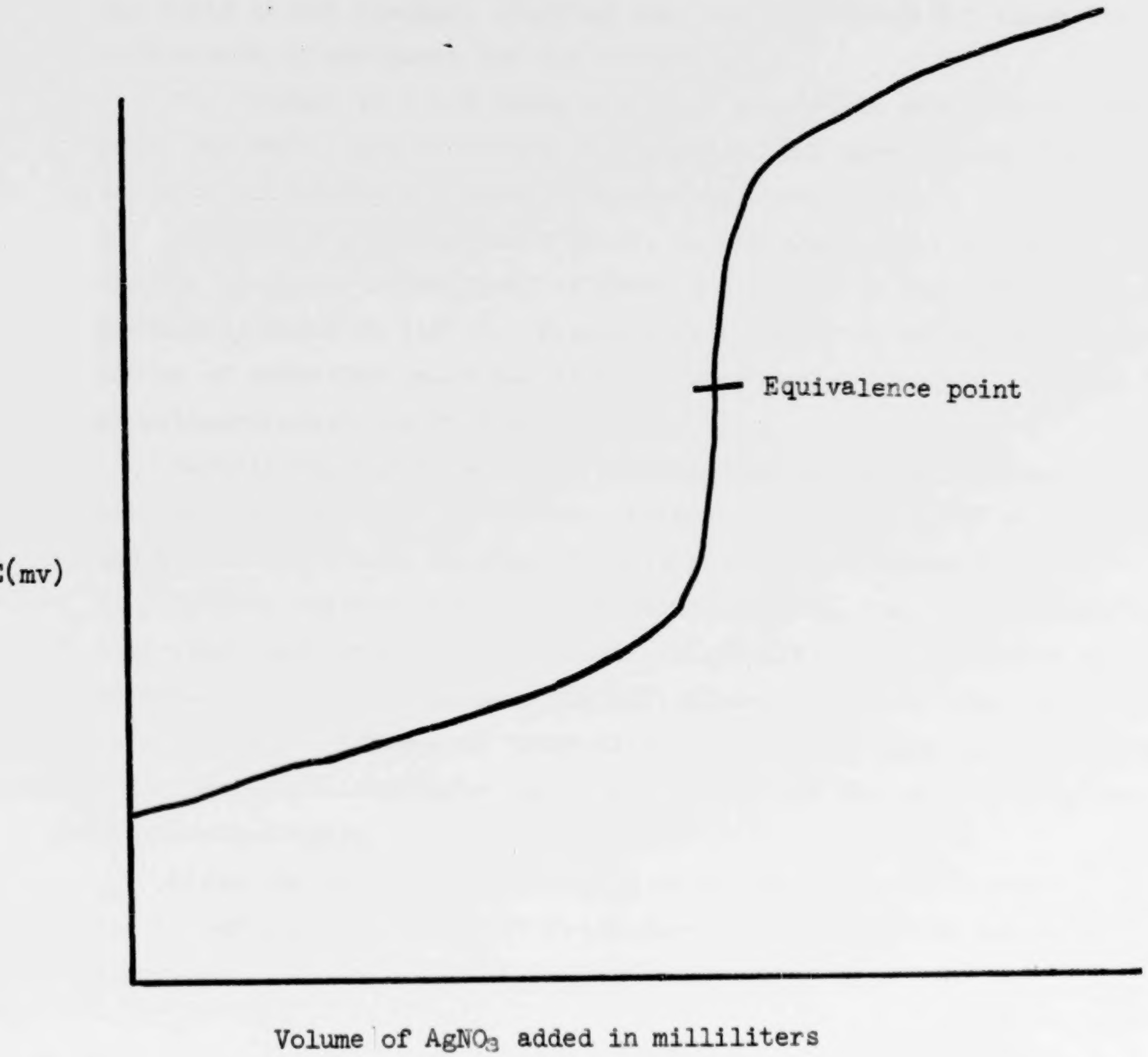


Fig. 5·2 Potentiometric titration of unknown chloride with standard AgNO$_3$

electrode use a glass electrode, but plug the electrode into the large, indicator terminal.* Caution: Keep the glass electrode immersed in pure water whenever not in use; avoid striking the glass bulb against any solid object (beaker, stirring bar, etc.). Figure 5·3 shows the arrangement of equipment for the titration.

The titrant is 0.1 M $AgNO_3$ solution, accurately standardized against pure, dry NaCl. See Procedures 5·2 and 5·3, but make up only 500 ml of solution containing 8.5 grams of analytical grade $AgNO_3$.

Into three 600-ml beakers weigh, to the nearest 0.1 mg, triplicate samples (properly identified) of about 0.5 g each of the unknown chloride, previously dried at 110° C. Dissolve each sample by adding approximately 300 ml of distilled water and stirring thoroughly. Analyze each solution potentiometrically as follows.

Immerse the electrodes into the solution and begin vigorous stirring with magnetic stir bar and motor. Activate the meter (1400 mv setting) and adjust the needle to read .2 volts prior to titration.**

Titrate the solution with the standard $AgNO_3$, taking potential readings after each addition of titrant. Start with increments of 4 ml, but decrease to about 0.2 ml near the equivalence point, so that each change in potential never exceeds 20-25 millivolts. Allow time for equilibration. After the equivalence point has been passed, the increments may gradually be increased again.

Rinse the electrodes thoroughly after each complete titration. Immerse the rinsed glass electrode in fresh pure water at the conclusion of the experiment.

---

*According to these directions the electrodes are attached to the pH meter in reverse manner, but this is completely satisfactory for the purposes of the experiment, because only differences between the two electrode potentials are to be measured. With electrodes assembled this way, the meter reading should increase as titration proceeds.

**The value chosen for this first reading is not important but it should be no greater than .6 volts, to make sure that the needle will remain on scale throughout the titration. In the analysis, great interest is placed only upon how the difference between the two electrode potentials changes as titration proceeds, not on the exact value of the difference.

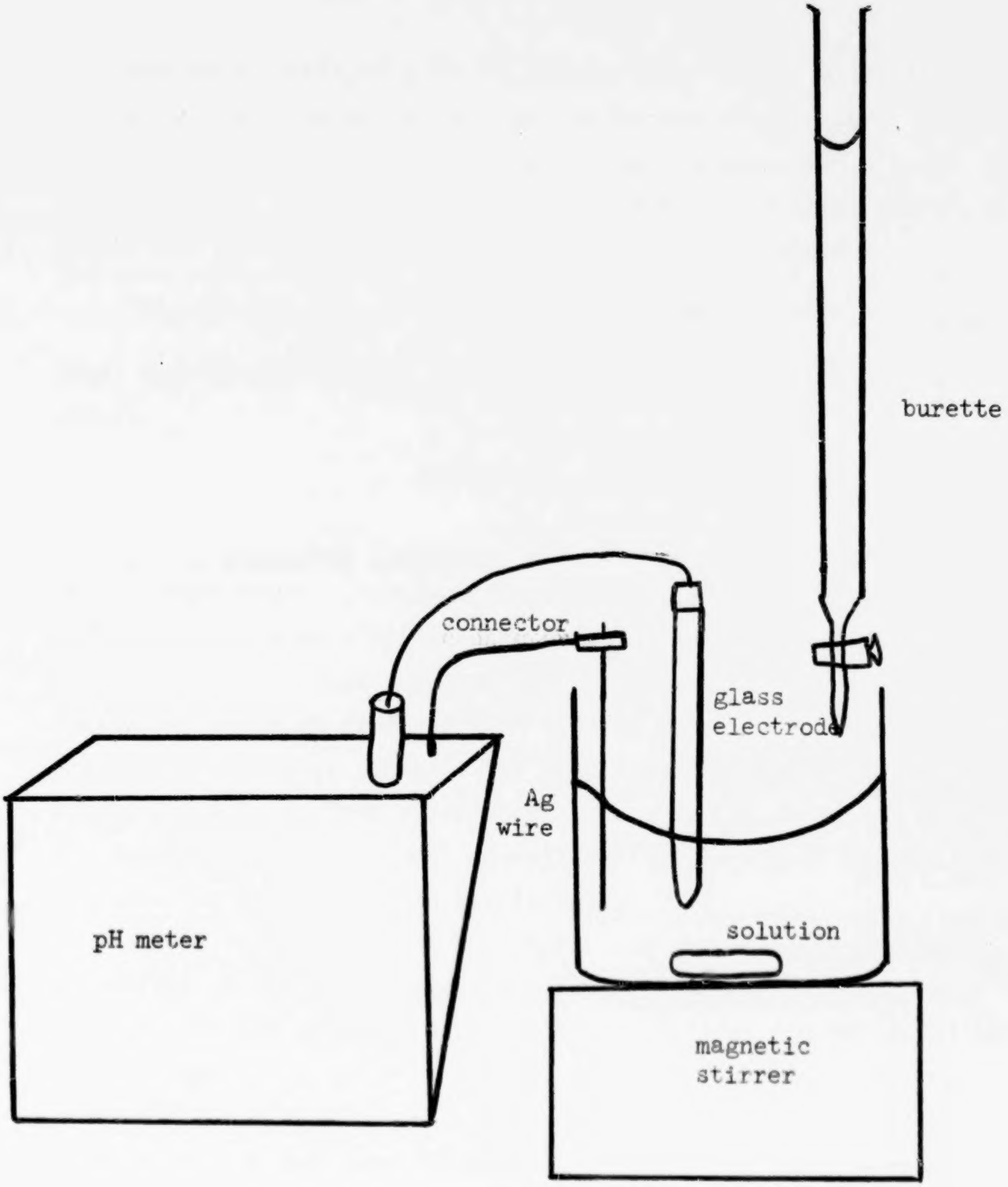

burette
connector
glass
electrode
Ag
wire
pH meter
solution
magnetic
stirrer

Figure 5·3 Apparatus for potentiometric titration.
(Ring stands and clamps are required to support the burette and electrodes.)

For each titration plot millivolts (emf) versus milliliters of silver nitrate titrant, using rectangular coordinate graph paper. The midpoint of the sharp break in the curve indicates the equivalence point of the titration (see Fig. 5·2). From the average of the three titrations, calculate the percentage of chloride in the unknown sample.

$$\frac{\text{ml of } AgNO_3 \times \text{M of } AgNO_3 \times 0.03545 \text{ g/mmole} \times 100}{\text{weight of sample in grams}} = \%\ Cl$$

Label your graphs completely and submit them along with your averaged result.

GRAVIMETRIC METHODS

5·7 Preliminary Comments. The word gravimetric has reference to a weight measurement; consequently, a gravimetric method is one in which an analysis is performed by means of weighing operations. More completely, a gravimetric analysis involves the determination of the weight of a pure substance, which is produced from a given weight of a sample. In the analytical procedure process, the sample is dissolved, and the substance sought is isolated from other constituents by the formation of an insoluble precipitate. Additional operations include the filtration and the ignition (or drying) of the precipitate.

Not all precipitates are suitable for gravimetric procedures. Consideration of the properties which render a precipitate adaptable to gravimetric work will be reserved for theoretical discussion elsewhere; as for example, solubility, purity, filterability, and stability. Even under optimum conditions, the procedures of gravimetric precipitation are usually tedious and time-consuming. On the other hand, some gravimetric analyses are preferable to comparable volumetric determination because of greater accuracy. It is also true that many gravimetric precipitations are necessary because no other satisfactory methods are available.

The gravimetric analyses of chlorine in a soluble chloride, and that of iron in ferrous ammonium sulfate, have been selected as typical examples of gravimetric precipitations.

5·8 Gravimetric Determination of Chlorine in a Soluble Chloride. The chlorine content of a soluble chloride is precipitated from a slightly acid (HNO_3) solution as silver chloride: $Cl^- + Ag^+ = \underline{AgCl}$

When first precipitated, the AgCl particles are in a colloidal state, but they are readily coagulated -- when heated -- to produce a curdy precipitate. This type of precipitate is easily filtered, and may be readily washed free of impurities. The precipitation is carried out in an acid solution to prevent interference from anions of weak acids, such as carbonate ion, which would coprecipitate in neutral media. A moderate excess of silver ion is necessary to reduce the solubility of the precipitate, but a large excess may result in an error through excessive coprecipitation.

In the presence of strong light the silver chloride undergoes photodecomposition as follows:

$$\underline{AgCl} \xrightarrow{light} \underline{Ag} + Cl_2$$

The white precipitate turns violet in color due to the presence of finely divided particles of silver. The possible errors resulting from this decomposition are interesting. If the precipitate has been washed, the results will be low because of the loss of chlorine. On the other hand, if the photodecomposition takes place in the precipitating solution, the liberated chlorine molecules react with water and excess silver ions to produce additional AgCl. This will cause the analytical results to be too high. The reaction is as follows:

$$3\ Cl_2 + 3\ H_2O + 5\ Ag^+ = 5\ \underline{AgCl} + ClO_3^- + 6\ H^+$$

The error caused by photodecomposition is far greater in the precipitating medium than in the washed precipitate. Hence it is necessary to coagulate the precipitate as rapidly as possible, and to protect it from light during the aging process.

Some photodecomposition is unavoidable, but with proper precautions the total error is small. After the washed precipitate is dried, additional decomposition is negligible.

It is customary to filter and wash the AgCl through either a Gooch crucible or a sintered-glass crucible. The latter is more convenient to use, but it is difficult to clean, and should not be heated much above 100° C.

Preparation of Crucibles. Three Gooch crucibles are to be used in the analysis. Before preparing the asbestos mats, examine the crucibles for distinguishing marks. If none are found, mark the unglazed bottoms with identifying letters, or numbers, using a special (heat insensitive) marking pencil; heat to redness in a colorless flame, and allow to cool in the desiccator.

Prepare asbestos mats in the Gooch crucibles as directed in Sec. 3·2. It is essential that these mats be made properly. The asbestos soup should be fairly thin and the resulting mats must be uniform in appearance, and of suitable thickness. An unsatisfactory mat may cause the total loss of many hours of work involved in the determination.

Wash the mats thoroughly with distilled water, using a gentle suction, until no loose fibers emerge with the washings. Test by collecting a portion of wash water in a clean test tube. Place each crucible in a small beaker, and dry in oven at 110° C for 1 hour. Cool in desiccator, and weigh. Repeat the drying, cooling, and weighing procedure until each crucible has reached constant weight (within 0.0003 g).* Keep complete record of all weighings. The crucible is now ready for use.

Sintered-glass crucibles of medium or fine porosity may be used in place of the Gooch filters. If crucibles are not new, remove visible dirt with detergent and water. Place in crucible holder and fill about halfway with concentrated nitric acid; draw through mat with gentle suction. Repeat once again with nitric acid, and then wash several times with water. If crucible mat is not clean, discard washings from filter flask, and repeat washing operations using 6 M ammonia. Rinse several times with distilled water. Dry crucibles in oven, and bring to constant weight.*

Procedure. Dry the impure chloride at 110° C for at least one hour. Weigh out (to 0.1 mg) three samples between 0.3 and 0.4 g into 400-ml beakers (properly identified). Dissolve in approximately 100 ml of distilled water and add about 1 ml of concentrated nitric acid.** To

*Drying and cooling periods should be approximately the same; otherwise, it will be difficult to attain constant weight. For example, if the crucible is dried for one hour and permitted to cool 20 minutes, the same intervals should be used when the procedure is repeated.

**Nitric acid aids in coagulating the precipitate; it also reduces coprecipitation.

the cold solution, add slowly, with constant stirring, 80 ml of your 0.1 M $AgNO_3$ solution (previously prepared in Sec. 5·2). Cover with watch glass, and heat nearly to boiling; continue to heat gently until the precipitate is coagulated. Test for complete precipitation by adding a few drops of $AgNO_3$ solution. Avoid exposing the beaker (containing precipitate and solution) to light any longer than necessary. Store in desk overnight, and keep in darkened area until ready for filtering.

Prepare a wash solution by adding about one ml of concentrated nitric acid to 500 ml of distilled water contained in the wash bottle.

Place a prepared filtering crucible in the filter holder as indicated in Fig. 3·1, and apply gentle suction. Carefully decant the liquid above the AgCl precipitate through the filter. Guide the liquid into the crucible by means of a glass rod as shown in Fig. 5·1, retaining as much of the precipitate in the beaker as possible.

Add roughly 25 ml of wash solution to the precipitate in the beaker, stir well, and allow to settle. Decant the washing through the filter, still retaining the bulk of precipitate in beaker. Repeat the washing procedure once more, then transfer the precipitate to the filter with the aid of a stirring rod and a stream from wash bottle (Fig. 5·1). Particles clinging to the beaker may be scrubbed away by means of a rubber policeman on the end of a stirring rod. Wash such particles into the filter.

Detach the funnel (including the filter and support ring) from the filter flask; insert the funnel into the mouth of a clean test tube. Add 2 or 3 ml of wash water, and allow the water to drip into the tube. Test for complete washing by adding a drop of hydrochloric acid to the filtrate in the test tube. If no cloudiness occurs, the precipitate has been washed sufficiently. In case of cloudiness continue the washing with wash solution until the test produces no cloudiness.

Dry the crucible and contents (in a small beaker) at 110° C until constant weight is attained (within 0.0003 g). Drying and cooling periods should be approximately the same as before: dry for one hour, cool for 20 minutes, and then weigh. Record all data.

Calculations. Compute the weight percentage of chloride by multiplying the gravimetric factor $Cl/AgCl$, times the ratio of the dried precipitate over the weight of sample, as follows:

$$\frac{Cl}{AgCl} \times \frac{\text{wt. of dried ppt. in grams}}{\text{wt. of sample in grams}} \times 100 = \%\ \text{chlorine}$$

5·9 The Gravimetric Analysis of Iron in Ferrous Ammonium Sulfate. The gravimetric analysis of iron in any type of mineral is a time-consuming process, which may contain a number of pitfalls. On the other hand, the gravimetric determination of iron in an impure salt is relatively simple and straightforward; it gives the student the experience of dealing with a gelatinous precipitate without the pitfalls attendant to the analysis of a mineral.

Ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, containing known quantities of impurities, is selected for analysis because of three desirable properties: (1) relatively high chemical stability, (2) convenience in handling, and (3) solubility in slightly acid solution.

The iron salt must not be dried in the oven because at an elevated temperature the ferrous ion is slowly converted to the ferric state before weighing, thereby introducing a significant error.

The ferrous salt is weighed, and then dissolved in distilled water which has been acidified with hydrochloric acid. In contact with air, the iron in ferrous salt solutions is slowly oxidized by dissolved oxygen,

$$4\ Fe^{++} + O_2 + 2\ H_2O = 4\ Fe^{+++} + 4\ OH^-$$

and unless the solution contains excess hydronium ions (to remove hydroxide ions) the iron will be partially precipitated in the form of ferric basic sulfate:

$$Fe^{+++} + OH^- + SO_4^= = \underline{Fe(OH)SO_4}$$

The addition of HCl prevents this precipitation.

The ferrous ion is oxidized to the ferric ion with nitric acid as is indicated by the following equation:

$$3\ Fe^{++} + NO_3^- + 4\ H^+ = 3\ Fe^{+++} + NO + 2\ H_2O$$

Iron in the ferrous state cannot be completely precipitated with ammonia, whereas iron as the ferric ion may be precipitated quantitatively even in a slightly acid solution. For gravimetric precipitation, iron is always oxidized to the +3 oxidation state.

When iron, in the tripositive state, is treated with ammonia, it is quantitatively precipitated as hydrous ferric oxide,

$$2\ Fe^{+++} + 6\ NH_3 + xH_2O = \underline{Fe_2O_3 \cdot xH_2O}$$

The precipitate is so gelatinous in nature that it can be regarded as a flocculated colloid. The enormous surface presented by the primary particles is conducive to extensive contamination by adsorption. Since the precipitate cannot be purified appreciably by digestion, it is necessary to resort to double precipitations to remove nonvolatile contaminants.

If the precipitate formed in the ammonia treatment is regarded as $Fe(OH)_3$, it is stabilized by the primary adsorption of hydroxide ions, and the secondary adsorption of any cations (M^+ or M^{++}) which may be present in solution. Consequently, the flocculated particle may be represented as: $Fe(OH)_3 \cdot OH^- \ldots M^+$ (or M^{++}). If a large excess of ammonium ions is present in the precipitating and wash solutions, the counter ion (M^+), during and after the double precipitations, will be largely the ammonium ion. The precipitate can then be indicated as: $Fe(OH)_3 \cdot OH^- \ldots NH_4^+$. Since the ammonium ion is volatilized during the ignition of the washed precipitate, little or no error results from this adsorption.

The precipitate is finally ignited to and weighed as the oxide:

$$Fe_2O_3 \cdot xH_2O \longrightarrow Fe_2O_3 + xH_2O$$

The ignition requires considerable care: the paper must be burned off slowly, with a good circulation of air in the crucible to prevent reduction of the ferric oxide, and the final temperature (about 850° C) must be sufficiently high to remove all water from the oxide.

Preparation of Crucibles. Three porcelain crucibles are to be used as containers for the ignition of the precipitates of hydrous ferric oxide. These crucibles are relatively stable up to 1000° C in the absence of alkalies, alkali carbonates, or fluorides. Above 1000° C, the porcelain glaze melts, and the bodies of the crucibles will begin to soften. An ordinary Tirrill burner (a doubly regulated Bunsen burner) does not give a sufficiently high temperature for ignition. It is customary to use either a Meker burner, or a muffle furnace to attain the desired temperature of about 850° C.

Examine the crucibles for identifying marks, and if none are found, mark the unglazed bottoms with your initials and a sequence of numbers, using a special, heat-resistant marking pencil. Check for hidden cracks in the crucibles.* Heat the bottoms of the dry crucibles to redness in a colorless flame produced by a Tirrill burner, and allow to cool in the desiccator. Iron stains within a crucible from previous determinations do not affect the present analysis.

Bring the crucibles to constant weight (within 0.3 mg) by placing them in a muffle furnace for twenty minutes; allow to cool in open air for 3 minutes (no more), and then cool in desiccator for twenty minutes. Each of the heating and cooling intervals should be the same; otherwise, it may be difficult to get the crucibles to constant weight. If a muffle furnace is not available, a Meker burner may be used.

Precipitation and Filtration. The unknown samples are not to be dried. Weigh out (to 1 mg) three samples between 2.0 and 3.0 g into 400-ml beakers. To each portion add 50 ml of water and 5 ml of concentrated hydrochloric acid; heat until samples are dissolved. Continue to heat until the solutions are boiling, and then add about 30 drops of concentrated nitric acid, drop by drop, by means of a pipette, until the darkened liquid clears to a yellow. Continue to boil for 3 minutes to expel the oxides of nitrogen. Dilute the solution to 200 ml; heat again to boiling, and add slowly with stirring (from graduate) 25 ml of 6 M ammonia. (If the ammonia water from the reagent bottle is not perfectly clear, it should be filtered; otherwise, silica from the glass bottle will cause an appreciable error in the analysis.) After the precipitation is complete, a strong odor of ammonia should persist above the solution. If not, add more ammonia. Continue to digest for about 1 minute; then, without delay, decant the clear supernatant liquid through a coarse-grained "ashless" 11-cm filter paper (Whatman No. 41 or equivalent) into a 600-ml beaker, keeping as much as possible of the precipitate in the original beaker. Add to the original beaker 50 ml of ammonium nitrate wash solution (1 g of ammonium nitrate per 100 ml of water), heat, and decant the hot washing through the filter paper. Repeat the washing procedure once more, then remove the 600-ml beaker and discard the clear filtrate.

---

*A sound crucible -- without lid -- produces a distinct ringing tone when dropped onto its base from a height of half-an-inch. An infirm crucible produces only a dull thud.

Place the original 400-ml beaker (containing the bulk of the precipitate) under the filtering funnel. Take care not to get different samples mixed. Now pour 10 ml of 6 M HCl slowly over the filter, so as to dissolve completely any precipitate on the filter. Wash the filter two or three times with hot water. When the last wash water has drained into the beaker, dilute to 200 ml. (If you do not have at least one hour available to complete the double precipitation, stop at this point, and store beaker covered with watch glasses in your desk.) Precipitate once again by adding an excess of ammonia, which should be approximately 25 ml of 6 M ammonia. Repeat the filtration, this time transferring the precipitate quantitatively to the filter paper during the washing operations. Rub loose any particles adhering to the beaker with a rubber policeman attached to the end of the stirring rod. Continue washing the precipitate with hot wash water, containing ammonium nitrate, until a 5 ml portion of the wash water passing through the filter paper gives only a faint cloudiness with silver nitrate. Once started, the filtration cannot be interrupted, because if the hydrous ferric oxide dries, the surface cracks, and washing becomes ineffective. Wipe the beaker with a small piece of dry ashless filter paper to remove the last traces of the precipitate, and add the filter paper to the precipitate in the funnel. Allow the filter and its contents to drain thoroughly. Fold the edge of the filter paper inward to cover the precipitate, then lift it carefully from the funnel, and place upside down in a previously ignited and weighed crucible.

Ignition of Precipitate in Paper. The crucible and its contents are placed in a beaker (covered with a watch glass), and dried in the oven for about 20 minutes, or overnight if convenient. The crucible with cover is next set in a triangle on a ring stand and heated over a low Tirrill flame. The height of the flame is increased gradually to carbonize the paper. The crucible is kept covered during the carbonization, but the cover may be lifted to observe the progress of charring. The paper must not be allowed to burst into flame. When the paper is completely charred, as revealed by its black color, remove the cover, and transfer the uncovered crucible to a muffle furnace. Bring the crucible and contents to constant weight (within 0.3 mg). The time intervals for heating and cooling should be the same as used in getting the crucibles to constant weight: heat 20 minutes; cool in open air 3 minutes, and then cool in desiccator for 20 minutes. When placed in the desiccator, the crucible should be covered; otherwise, a partial vacuum in the desiccator produced by the cooling crucible, may cause the contents of the crucible to be sucked out when the top of the desiccator is removed. Always slide the top of the desiccator slowly when opening it.

In the absence of a muffle furnace, a Meker burner may be used in bringing the crucible and its contents to constant weight.

Calculations. The iron content of the original sample is obtained by multiplying the gravimetric factor, 2 Fe/Fe_2O_3, times the weight of ignited precipitate over the weight of the sample, as follows;

$$\frac{2\ \mathrm{Fe}}{\mathrm{Fe_2O_3}} \times \frac{\text{wt. of ignited ppt. in grams}}{\text{wt. of sample in grams}} \times 100 = \%\ \text{iron}$$

Appendix

INSTRUCTIONS FOR OPERATIONS OF pH METERS

A·1 Beckman Zeromatic pH Meter, 9600 Series. General: The instrument is sketched in Fig. A·1. At the front of the meter, the three pairs of buttons are switches for joining various parts of the circuitry:

(1) The pH controls (MAN. and AUTO.) are used only during pH measurements.

The MAN. button allows manual temperature regulation (using the upper left control dial).

The AUTO. button is used only in conjunction with an automatic thermo-compensator unit.

(2) The MILLIVOLT controls (±700 and 1400) are used only during emf (millivolt) measurements.

The ±700 button is used when one wishes to measure the absolute potential difference (in millivolts) between two electrodes; the voltmeter scale reads only from +.7 volts to -.7 volts, a total span of 1.4 volts, with the "zero" position on the scale automatically reset once every second to correspond exactly to a potential difference of zero volts.

The 1400 button also provides a total voltage span of 1.4 volts but the "zero" may be set manually (lower left control dial) to correspond to any emf value desired.

(3) The ELECTRODE controls connect and disconnect the electrodes from the measurement circuitry.

Keep STANDBY depressed except when taking readings.

Depress READ only during measurements when electrodes are in contact with liquid to be measured; a "clicking" should be heard when READ button is down.

The 0 to 14 scale on the voltmeter is used for determining pH, or for measuring emf with the 1400 button. The +7 to 0 to -7 scale is used in conjunction with the ±700 button in emf measurement.

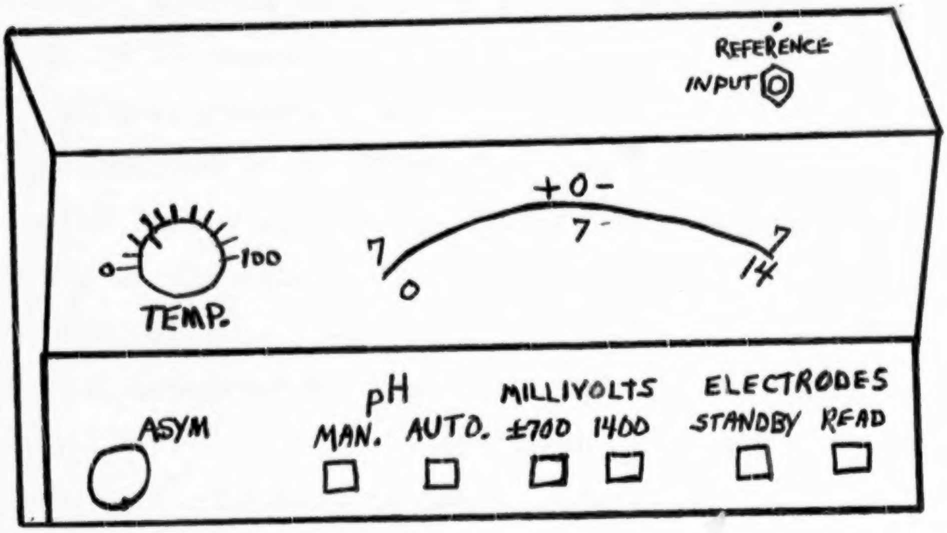

REFERENCE
INPUT
+ 0 -
7
7
7
0
14
0
100
TEMP.
pH
MILLIVOLTS
ELECTRODES
ASYM
MAN.
AUTO.
±700
1400
STANDBY
READ

Figure A·1 Beckman Zeromatic pH meter, 9600 series.

The TEMP. control dial, used only for pH measurements (inoperative during emf measurements), electronically compensates for the temperature of the solution being measured (range 0 to 100° C). In effect, it adjusts the value of the coefficient $(-\frac{2.303RT}{n\mathcal{F}})$ in the equation:

$$E_{\text{glass electrode}} = E' + \frac{2.303RT}{n\mathcal{F}} \log a_{H^+}$$

so that the scale spacing of the meter is accurately calibrated for changes in $(-\log a_{H^+})$.

The ASYM. control knob, in effect, electronically accounts for the value of E' in the equation above.

> In pH measurement, the ASYM. knob is adjusted while the electrodes are immersed in a buffer solution of known pH, until the meter needle points to that pH value. This adjustment brings the meter needle into accurate position with respect to the scale of the meter.
>
> In emf measurement, the ASYM. knob is used only in conjunction with the 1400 button (inoperative with ±700 button), to vary the "zero" position on the millivolt scale.

The electrodes plug into the right rear of the instrument. The glass electrode fits into the larger opening. (The instrument is designed for only Beckman glass electrodes, but devices for connecting other types of electrodes are available commercially.) Any glass electrode which has been left out of water for an extended period of time must be re-conditioned before use, by immersing the electrode for at least two hours in a solution of pH 7 buffer or for several hours in pure water. The soaking is necessary to hydrate the special, soft glass at the electrode tip. The reference electrode may also need to be soaked to remove crystallized KCl from the fiber junction at the tip.

pH Standardization with Buffer Solution (without auto. temp. compensator): The meter must be standardized before each series of pH measurements, using a buffer solution of known pH. For accurate work, the pH of the chosen buffer should be within 2 pH units of the values expected for the unknown sample at its equivalence point, and the buffer temperature should correspond within ±10° C to the temperature of the unknown sample solution. Stepwise directions follow.

(1) Have available (in addition to a magnetic stirrer, stir bar, and buffer solution, which are provided with the instrument):
    a thermometer for measuring solution temperature;
    a wash bottle with distilled water for rinsing electrodes;
    a beaker for catching all rinse water;
    a beaker filled with pure distilled water in which to immerse the electrodes while not in use -- clearly labelled;
    a small beaker (or two) for the buffer solution(s) -- clearly labelled as to buffer; and
    any additional beakers needed for the unknown solutions being measured -- clearly labelled.

(2) Depress STAND-BY button. If unplugged, connect power cord to 115 v a-c outlet and wait 2 minutes for warm-up. (Transistorized models require no warm-up time.) Meanwhile attach the electrodes securely to the rear of the console.

(3) Rinse electrodes with distilled water, then immerse them in buffer solution of known pH. Electrodes must not contact stirring bar and walls of beaker.

(4) Depress MAN.; set TEMP. knob to temperature of buffer solution, after allowing for temperature equilibration.

(5) Depress READ; adjust ASYM. knob until METER needle indicates correct value for pH of buffer solution (0 to 14 scale). Unsteady readings indicate a loose electrode connection or a broken electrode.*

(6) Depress STAND-BY; rinse electrodes with distilled water. The meter is now standardized.

*NOTE: In case of damage to a fragile electrode, real or imagined, notify the instructor at once.

As a check on the accuracy of the pH reading, the instrument may be re-standardized with a second, different, buffer solution. The new pH reading should agree closely with the expected value for this buffer, without change in the ASYM. knob. Do not discard either buffer solution from its beaker until you have completed the ENTIRE pH experiment. Continue immediately with pH measurement of unknown sample, according to the following stepwise procedure.

pH Measurements on an Unknown Sample Solution: This procedure must be preceded by pH standardization (above).

(1) Immerse rinsed electrodes in sample solution under investigation; stir vigorously but without splashing -- the tips of the electrodes must remain submerged at least 10 mm.

(2) After temperature equilibration, set TEMP. knob to temperature of sample solution.*

(3) Depress READ, and record pH value of sample solution from METER (0 to 14 scale).

(4) Depress STAND-BY.

Repeat (3)-(4), as desired.

During titrations, keep the electrodes immersed in the solution while adding titrant. Allow a few moments for equilibration before taking new readings: steps (3)-(4) repeated.

(5) When ready to discard the solution, at completion of the titration, rinse the electrodes thoroughly and store them in distilled water. Leave pH meter plugged in, with STAND-BY depressed.

The above steps are followed anew for each additional titration on a new solution. The pH standardization of the instrument should be rechecked before and after each series of measurements, but not during a titration.

*There is often an appreciable temperature rise during pH titration, due to heat of neutralization and heat conduction from the stirring motor. This may be partially compensated for by inserting a water-bath-cooled plastic disc between the titration beaker and the stirring motor.

EMF Measurements in the +700 mv to -700 mv range: For such measurements, neither the TEMP. nor the ASYM. knobs are used. Have available (in addition to a magnetic stirrer, stir bar, and buffer solution, which are provided with the instrument):

a wash bottle with distilled water for rinsing electrodes;
a beaker for catching all rinse water;
a beaker filled with distilled water for immersing the electrodes when not in use -- clearly labelled;
any additional beakers needed for the unknown solutions being measured -- clearly labelled.

The stepwise procedure follows:

(1) Depress STAND-BY button. If unplugged, connect power cord to 115 v a-c outlet and wait 2 minutes for warm-up. Meanwhile attach the electrodes securely to the rear of the console.

(2) Rinse electrodes with distilled water, then immerse them in the unknown sample solution.

(3) Depress ±700 button.

(4) Depress READ, and record the emf value for the solution (using the +7 to 0 to -7 scale and multiplying by 100 to obtain mv units).

(5) Depress STAND-BY.

Repeat (4)-(5) as desired.

During titrations, keep the electrodes immersed in the solution while adding titrant; stir vigorously and continuously. Allow a few moments for equilibration before taking new readings by a repetition of steps (4)-(5).

(6) When ready to discard solution, after titration, rinse the electrodes thoroughly and store them in distilled water. Leave pH meter plugged in, with STAND-BY depressed.

Repeat the above six steps for each new titration or new solution analyzed. Unsteady readings indicate a loose electrode connection or a broken electrode. Notify instructor at once, in case of damage to a fragile electrode.

An emf value read with the ±700 button depressed, corresponds precisely to the true potential difference between the electrodes at the time of measurement.

EMF Measurements, using the 1400 button: For such measurements, the TEMP. knob is not used. The ASYM. knob adjusts the position of "zero" volts (emf) on the meter. Have available (in addition to a magnetic stirrer, stir bar, and buffer solution, arranged with the instrument) the same equipment listed for ±700 mv measurement. The stepwise procedure follows:

(1) Depress STAND-BY button. If unplugged, connect power cord to 115 v a-c outlet and wait 2 minutes for warm-up. Meanwhile attach the electrodes securely to the rear of the console.

(2) Rinse electrodes with distilled water, then immerse them in the unknown sample solution.

(3) Depress 1400 button.

(4) Depress READ; turn ASYM. knob until METER reading is set at a value satisfactory for the subsequent titration (so that all readings will be on scale during the titration); record the meter reading (using the 0 to 14 scale and multiplying by 100 to obtain mv units). Do not manipulate ASYM. knob for the remainder of the titration.*

(5) Depress STAND-BY.

*If a subsequent reading approaches the edge of the meter scale, add or subtract a definite number of millivolts from the reading, and reset the needle to the new position (using ASYM. knob). Make note of the change in emf reading, and correct all subsequent readings accordingly. The 1400 button is commonly used for emf titrations when true emf values are not required. Although the first reading (in millivolts) does not necessarily agree with the absolute millivolt potential difference between the electrodes, the meter scale does read relative millivolt units quite accurately, so that emf changes during titration can be measured with precision.

(6) To check the reading, depress READ, record the meter reading, then depress STAND-BY. Repeat check, as desired.

During titrations, keep the electrodes immersed in the solution while adding titrant; stir vigorously and continuously, but without splashing. Allow a few moments for equilibration, before taking new readings by step 6 procedure.

(7) When ready to discard solution, after titration, rinse electrodes thoroughly and store them in distilled water. Leave pH meter plugged in, with STAND-BY depressed.

Repeat the above seven steps for each titration on a new solution. Unsteady readings indicate a loose electrode connection or a broken electrode. Notify instructor at once in case of damage to a fragile electrode.

A·2. Leeds and Northrup pH Meter, Model 7401. General: The instrument is sketched in Fig. A·2. At the front of the instrument are four control knobs used to join together and calibrate various parts of the circuitry:

(1) The left-hand knob sets the desired function.

MAN. TEMP is used for pH measurements with temperature set manually (by adjustment of TEMPERATURE knob).

AUTO. TEMP is used for pH measurements only in conjunction with an automatic Thermohm compensator.

700 MV is used for millivolt measurements (e.g., redox titrations) when the actual difference in emf between the electrodes does not exceed ±700 mv.

1400 MV is used for millivolt measurements not exceeding ±1400 mv.

(2) The TEMPERATURE knob, used only for pH measurements, electronically compensates for the temperature of the solution being measured (range 0 to 100° C). In effect, it adjusts the value of the coefficient $(-\frac{2.303RT}{n\mathcal{F}})$ in the equation

$$E_{\text{glass electrode}} = E' + \frac{2.303RT}{n\mathcal{F}} \log a_{H^+}$$

so that the scale spacing of the meter is actually calibrated for changes in $(-\log a_{H^+})$.

(3) The ZERO & STANDARDIZATION knob is used to position the meter pointer correctly on the scale. In effect, it electronically accounts for the value of E' in the equation above. In pH measurement, it is adjusted while the electrodes are immersed in a buffer solution of known pH, so that the meter pointer is accurately positioned with respect to the scale on the meter. In emf measurement, the knob is used with both the 700 and the 1400 knobs to adjust the meter pointer to "zero" position on the millivolt scale. (Note that the "zero" position may be placed at either end of the meter scale, depending upon whether emf measurements are expected to be negative values or positive values.)

The ZERO & STANDARDIZATION knob is a combination of a coarse and a fine rheostat operated from the same shaft; a backlash vernier

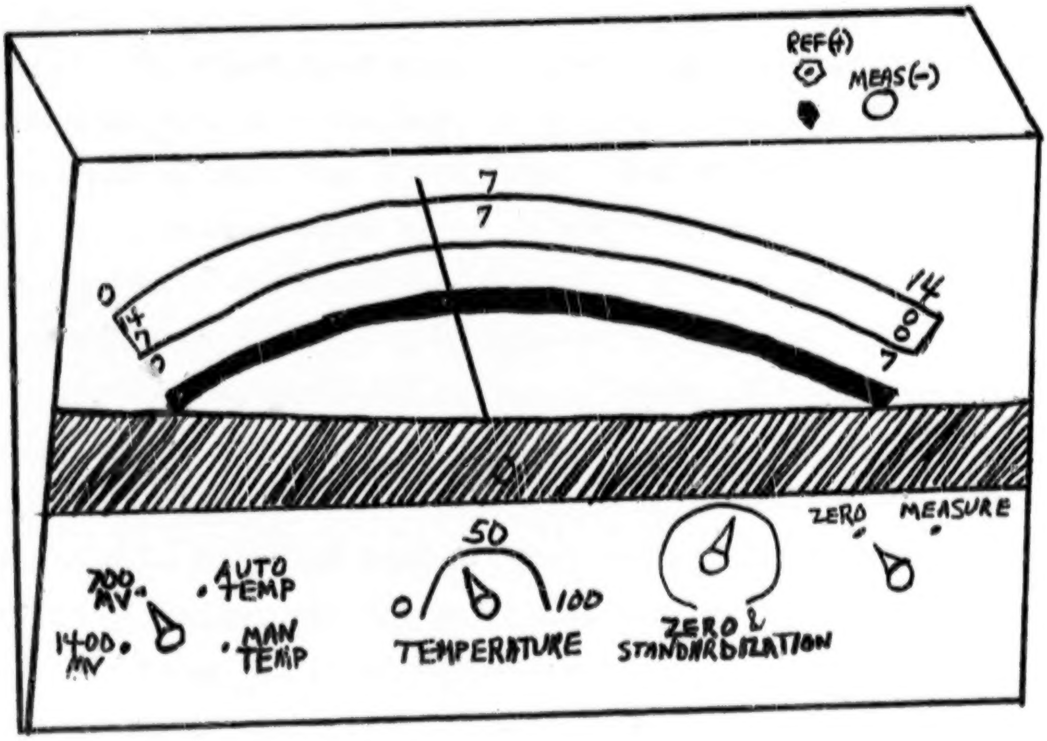

REF(+)
MEAS(-)
7
7
0
14
7
7
50
0
100
TEMPERATURE
ZERO & STANDARDIZATION
ZERO
MEASURE
700 MV
1400 MV
AUTO TEMP
MAN TEMP

Figure A·2 Leeds and Northrup Stabilized pH Indicator.

permits turning the fine rheostat a fixed distance in either direction before engaging the coarse rehostat. Therefore, in using the knob to set the meter pointer to a certain desired value, the knob is turned continuously -- in either direction -- until the meter pointer barely passes beyond the desired value (coarse control), then a slight reverse motion of the knob brings the pointer back to the desired reading (fine control). Remember this procedure when following the stepwise directions below.

(4) The right-hand knob connects and disconnects the electrodes from the measurement circuitry. Keep the switch on ZERO, except when making a reading with the electrodes. The MEASURE position is used only during actual measurements of pH or emf (not during setting of emf "zero") when electrodes are in contact with liquid to be measured.

The METER is provided with four different scales. For pH measurements, only the top scale (0 to 14) is read. For emf measurements at 700 MV position, the 0 to +7 scale is used (if "zero" has been set at left end of scale) or the -7 to 0 scale (if "zero" has been set at right end of scale -- negative values being recorded). For emf measurements at 1400 MV position, the corresponding scales to read are those from 0 to +14 and from -14 to 0, respectively.

The meter is also provided with a thin MIRROR beneath the scales.

To read the meter most accurately, close one eye, and align the meter pointer with its reflection in the mirrored surface, using the other eye. Your eye should then be positioned correctly for taking a precise reading on the meter scale. It is helpful to tap the meter case gently near the pointer screw immediately before taking a measurement.

The electrodes plug into the right rear of the instrument. The glass electrode fits into the larger opening, labelled MEAS(-). The other electrode fits into the small opening, labelled REF(+). The instrument is designed for Leeds and Northrup glass electrodes, but devices for connecting other types of electrodes are available commercially. Any glass electrode which has been left out of water for an extended period of time must be re-conditioned before use, by immersing the electrode for at least two hours in a solution of pH 7 buffer or for several hours in pure water.

pH Standardization with Buffer Solution (without automatic Thermohm compensator): The L and N meter must be standardized before each series of pH measurements, using a buffer solution of known pH. For accurate work, the pH of the chosen buffer should be within 2 pH units of the values expected for the unknown sample at its equivalence point, and the buffer temperature should correspond within ±10° C to the temperature of the unknown sample solution. Stepwise directions follow.

(1) If power cord is unplugged (and has been for at least 10 minutes), meter pointer should rest at pH 7.00. If it does not, have the instructor adjust the POINTER SCREW slightly. (This adjustment is rarely necessary except after a period of non-use or immediately after transporting an instrument to a new location.)

(2) Have available (in addition to a magnetic stirrer, stir bar, and buffer solution, which are provided with the instrument):

a thermometer for measuring solution temperature;
a wash bottle with distilled water for rinsing electrodes;
a beaker for catching all rinse water;
a beaker filled with pure distilled water in which to immerse the electrodes while not in use -- clearly labelled;
a small beaker (or two) for the buffer solution(s) -- clearly labelled as to buffer; and
any additional beakers needed for the unknown solutions being measured -- clearly labelled.

(3) Turn right switch to ZERO. If unplugged, connect power cord to 115 v a-c outlet and wait 2 minutes for warm-up. (Transistorized models require no warm-up time.) Meanwhile attach the electrodes securely to the rear of the console.

(4) Rinse electrodes with distilled water, then immerse them in buffer solution of known pH. Electrodes must not contact stirring bar and walls of beaker.

(5) Turn left switch to MAN. TEMP; set TEMP. knob to temperature of buffer solution, after allowing for temperature equilibration (about 5 minutes).

(6) Turn right switch to MEASURE; adjust ZERO & STANDARDIZATION knob until METER POINTER indicates correct value for pH of buffer solution (0 to 14 scale). Unsteady readings indicate a loose electrode connection or a broken electrode.*

(7) Turn right switch to ZERO; rinse electrodes with distilled water. The meter is now standardized.

(8) Record (for future reference) the present meter pointer reading (R_{zero} = ...) with the right hand switch at ZERO, and the temperature of the buffer (T_{buffer} = ...).

As a check on the accuracy of the pH reading, the instrument may be re-standardized with a second, different, buffer solution. The new pH reading should agree closely with the expected value for this buffer, without change in the ZERO & STANDARDIZATION knob. _Do not discard either buffer solution from its beaker until you have completed the ENTIRE pH experiment_. Continue immediately with pH measurement of unknown sample, according to the following stepwise procedure.

pH Measurements on an Unknown Sample Solution: This procedure must be preceded by the pH standardization (above).

(1) Immerse rinsed electrodes in sample solution under investigation; stir vigorously but without splashing -- the tips of the electrodes must remain submerged at least 10 mm.

(2) After temperature equilibration, set TEMP. knob to temperature of sample solution.** Record this temperature (T_{sample} = ...) for possible future reference.

*_NOTE_: In case of damage to a fragile electrode, read or imagined, notify the instructor at once.

**There is often an appreciable temperature rise during pH titration, due to heat of neutralization and heat conduction from the stirring motor. This may be partially compensated for by inserting a water-bath-cooled plastic disc between the titration beaker and the stirring motor.

(3) Turn right knob to MEASURE, and record pH value of sample solution from METER (0 to 14 scale).

(4) Reset right knob to ZERO.

Repeat (3)-(4), as desired.

During titrations, keep the electrodes immersed in the solution while adding titrant. Allow a few moments for equilibration before taking new readings: steps (3)-(4) repeated.

(5) When ready to discard the solution, at completion of the titration, rinse the electrodes thoroughly and store them in distilled water. Leave pH meter plugged in, with right knob at ZERO.

The above steps are followed anew for each additional titration on a new solution.

(For a simple recheck of the pH standardization at any time during a series of measurements (L and N pH meters only), set right knob at ZERO, and set TEMPERATURE knob at the value T_{buffer}. The meter pointer should then read the value R_{zero}; if it does not, the ZERO & STANDARDIZATION knob may be turned slightly so as to readjust meter needle to R_{zero}. The TEMPERATURE knob is then returned to the value T_{sample}, and measurement is resumed.)

EMF Measurements: For such measurements, the TEMPERATURE knob is not used. Have available (in addition to a magnetic stirrer and stir bar which are provided with the instrument):

a wash bottle with distilled water for rinsing electrodes;
a beaker for catching all rinse water;
a beaker filled with distilled water for immersing the electrodes when not in use -- clearly labelled;
any additional beakers needed for the unknown solutions being measured -- clearly labelled.

The stepwise procedure follows:

(1) Set right switch at ZERO. If unplugged, connect power cord to 115 v a-c outlet and wait 2 minutes for warm-up. Meanwhile attach the electrodes securely to rear of console.

(2) Rinse electrodes with distilled water, then immerse them in the unknown sample solution.

(3) Set left switch to 700 or 1400 (depending upon the range of emf readings needed for your study: respectively ±700 mv or ±1400 mv).

(4) Adjust ZERO & STANDARDIZATION knob until meter POINTER reads zero (at either the left or right end of the scale, depending upon whether the emf readings will be, respectively, positive or negative in value).

(5) Set right switch to MEASURE, and record the emf value for the solution. Be sure to use the correct scale on the meter, depending upon settings (3) and (4) above.

If the pointer reads off scale, make new settings (via steps 3 and 4 above) until a satisfactory measurement is obtained.

During titrations, keep the electrodes immersed in the solution while adding titrant; stir vigorously and continuously but without splashing. Allow a few moments for equilibration before taking new readings by a repetition of steps (3)-(4)-(5).

(6) When ready to discard solution, after titration, rinse the electrodes thoroughly and store them in distilled water. Leave pH meter plugged in, with right switch at ZERO.

Repeat the above six steps for each new titration or new solution analyzed. Unsteady readings indicate a loose electrode connection or a broken electrode. Notify instructor at once, in case of damage to a fragile electrode.

Both the 700 and 1400 settings provide emf values corresponding precisely to the actual potential difference between the electrodes at the time of measurement.

EQUIPMENT AND CHEMICALS

A·3 List of Equipment

Returnable items

2	Beakers, 50 ml
2	Beakers, 150 ml
2	Beakers, 250 ml
2	Beakers, 400 ml
2	Beakers, 600 ml
1	Bottle, 5 pint, plastic top
1	Bottle, 2 liter, unstoppered
2	Bottles, 1 liter, glass-stoppered
1	Bottle, 1/2 liter, glass-stoppered
1	Bottle, 250 ml, wide-mouth
3	Bottles, weighing
1	Brush, test tube
2	Burets, 50 ml
2	Burners, Tirrill, natural gas
1	Casserole, porcelain, 210 ml
1	Clamp, Hoffman, screw type
1	Clamp, test tube
3	Crucibles, porcelain, No. 0
3	Crucible covers, porcelain, No. 0
3	Crucibles, Gooch, porcelain, No. 3
1	Crucible holder, rubber ring for Gooch
1	Cylinder, graduated, 25 ml
1	Cylinder, graduated, 100 ml
1	Desiccator, with procelain plate
3	Flasks, Erlenmeyer, wide-mouth, 500 ml
1	Flask, filtering, side-arm, 500 ml
1	Flask, Florence, flat-bottom, 500 ml
1	Flask, volumetric, 250 ml
1	Flask, volumetric, 1000 ml
3	Funnels, fluted, long stem, 65 mm
4	Glass rods, stirring, 125 x 4 mm
1	Lock, combination, with hasp
1	Pipet, volumetric, 25 ml
1	Rubber stopper, solid, No. 7 or 8
1	Rubber stopper, 1-hole, No. 7 or 8
1	Rubber stopper, 2-hole, No. 7 or 8
1	Rubber stopper, 2-hole, No. 5
2	Rubber tubing, (1/4 x 3/32), 3 ft lengths for burners
1	Rubber tubing, (1/4 x 3/32), 3 ft length, utility
2	Rubber tubing, (1/4 x 3/16), 3 ft lengths, suction, thick wall
1	Spatula, micro
1	Support, funnel, wood, with clamp
4	Test tubes, 150 x 20 mm
1	Thermometer, 110° C
1	Tongs, crucible, cadmium plated steel
2	Triangles, nichrome, wire
2	Tripods, iron, threaded legs
2	Watch glasses, 50 mm
2	Watch glasses, 100 mm
2	Watch glasses, 150 mm
2	Wire gauzes, 100 x 100 mm
1	Wing top for burner

A·3 List of Equipment (continued)

Nonreturnable items

2	Corks, No. 2
1	File, triangular
1	Labels, box
1	Litmus, paper, blue, vial
1	Litmus, paper, red, vial
4	Matches, boxes
1	Pencil, wax
3	Rubber policemen
2	Rubber shock absorbers for graduates
1	Sponge
2	Towels
2	Tubes, glass, 750 x 6 mm

General Equipment

Asbestos gloves
Balances, analytical
Balances, triple beam
Buret holders, double, castaloy
Colorimeters (with cuvettes)
Filter paper, Quantitative (11 cm, various porosities)
Flasks, Erlenmeyer, 250 ml
Furnace, muffle
Oven, drying
pH meters (pH and millivolt scales)
Ringstands, with porcelain base
Stirrers, magnetic, (with coated bars)
Tongs for muffle furnace
Wiping tissue

A.4. Acids and Bases

Acetic acid, 17 M	Glacial acetic acid
Acetic acid, 6 M	360 ml of glacial acetic acid in a liter of solution
Ammonia, 15 M	Concentrated NH_3
Ammonia, 6 M	400 ml of concentrated NH_3 in a liter of solution
Hydrochloric acid, 12 M	Concentrated hydrochloric acid
Hydrochloric acid, 6 M	500 ml of concentrated HCl in a liter of solution
Nitric acid, 15 M	Concentrated nitric acid
Nitric acid, 6 M	375 ml of concentrated HNO_3 in a liter of solution
50% Sodium hydroxide, 19 M	Concentrated sodium hydroxide
Sodium hydroxide, 1 M	50 ml of concentrated NaOH in a liter of solution
Sulfuric acid, 18 M	Concentrated sulfuric acid
Sulfuric acid, 3 N	160 ml of concentrated H_2SO_4 in a liter of solution
Sulfuric acid, 1.5 N	80 ml of concentrated H_2SO_4 in a liter of solution

A·5 Reagent Solutions

Ammonium oxalate, 0.25 M	35.5 g of $(NH_4)_2C_2O_4 \cdot H_2O$ dissolved in water and diluted to 1 liter
Asbestos suspension	4 g of asbestos in 800 ml of distilled water contained in a liter bottle
Cleaning solution	20 g of $Na_2Cr_2O_7 \cdot 2H_2O$ in hot, concentrated H_2SO_4 (not more than 100° C)
Hydroquinone, 1%	10 g dissolved in water and diluted to 1 liter
Mercuric chloride, saturated	70 g of $HgCl_2$ added to 1 liter of water
1,10-Phenanthroline, 0.5%	5 g of the monohydrated dissolved in water and diluted to 1 liter
Silver nitrate, 0.1 M	17 g of $AgNO_3$ dissolved in water and diluted to 1 liter
Sodium citrate	250 g of the dihydrate dissolved in water and diluted to 1 liter
Stannous chloride	56 g of $SnCl_2 \cdot 2H_2O$ dissolved in 100 ml of conc. HCl, allowed to stand until clear, and then diluted to 1 liter, with addition of a few pieces of metallic tin to the solution
Zimmermann-Reinhardt (preventive solution)	Dissolve 1 lb of $MnSO_4 \cdot H_2O$ in 3 liters of water, and combine with a cooled mixture of 600 ml of H_2SO_4 and 600 ml of H_3PO_4 in 1800 ml of H_2O

A·6 Indicator Solutions

Bromcresol green	Dissolve 0.4 g bromcresol green in 6 ml of 0.1 N NaOH and dilute to 1 liter
Dichlorofluorescein	Dissolve 1 g of dichlorofluorescein in 1 liter of ethanol
Methyl red	Dissolve 0.4 g of methyl red in 15 ml of 0.1 N NaOH and dilute to 1 liter
Mixed indicators	Mix 2 parts of methyl red solution with 3 parts of bromcresol green solution
Potassium chromate, 0.1 M	19.4 g of K_2CrO_4 dissolved in water and diluted to 1 liter
Starch indicator	Stir 2 g of "soluble" starch with 20 ml of water in a small beaker to form a paste. Pour the paste slowly into 500 ml of boiling water. Add 0.02 g of HgI_2 as preservative.

A·7 Solid Reagents and Their Uses

Reagent	Use
Ammonium nitrate	Gravimetric iron
Calcium chloride	Desiccator
Dextrin	Volumetric chloride
Iodine	Antimony
Potassium iodide	Antimony
Potassium permanganate	Iron and calcium
Potassium sodium tartrate	Antimony
Potassium thiocyanate	Copper
Sodium bicarbonate	Antimony
Sodium thiosulfate	Copper
Stopcock grease	Buret
Urea	Copper
Vaseline	Desiccator

A·8 Primary Standards and Their Uses

(These reagents should have a purity of 99.90 per cent of better.)

Standard	Use
Arsenious oxide	Standard iodine
Copper, metal	Standard copper
Ferrous ammonium sulfate	Standard iron
Potassium acid phthalate	Standard base
Sodium chloride	Standard $AgNO_3$
Sodium oxalate	Standard $KMnO_4$

A·9 Unknown Substances for Analysis

(These materials may be obtained from Thorn Smith, 847 North Main Street, Royal Oak, Michigan.)

Calcium carbonate

Copper oxide

Ferrous ammonium sulfate

Iron ore

Potassium acid phthalate

Soda ash

Soluble antimony

Soluble chloride

FINAL REPORT

Cooperate Research Project No. S-419-66 Contract OE-5117

Period covered by report: September 15, 1965 to August 15, 1966

Name of institution:	Washington and Lee University, Lexington, Va. 24450
Title of project:	The Development of Laboratory Procedures for a Course in Elementary Quantitative Chemistry on a Freshman Level, with Some Emphasis on Instrumental Methods of Analysis.
Name of project directors:	Esmarch S. Gilreath (Principal Investigator) J. Brown Goehring (Associate) William J. Watt (Associate)

(The following pages contain the materials requested for a standard report.)

5-8337

THE DEVELOPMENT OF LABORATORY PROCEDURES FOR A COURSE IN ELEMENTARY QUANTITATIVE CHEMISTRY ON A FRESHMAN LEVEL, WITH SOME EMPHASIS ON INSTRUMENTAL METHODS OF ANALYSIS

Cooperative Research Project No. S-419-66   Contract OE-5117

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PRECEDING PAGE MISSING

4. Problem on which research was focused.

Our problem has been the development of a laboratory program in quantitative chemistry, suitable for freshman pre-medical and other science students, retaining the emphasis upon precise laboratory technique usually associated with sophomore quantitative analysis courses, but providing training in the use of essential instruments of analytical chemistry. One particular aspect of this problem is that of integrating the use of instruments with classical quantitative techniques.

5. Objectives and/or hypothesis.

The main objective was to produce a manual containing laboratory procedures for a one-semester course in elementary quantitative chemistry on a freshman level. The authors recognize the fact that the high school training in chemistry of entering college freshmen has improved significantly within recent years. Consequently, the laboratory procedures have been developed for those freshmen who have a good background in high school chemistry.

The procedures have been written in a form which can be easily followed by either students or teachers.

The authors believe that spectrophotometric instruments and pH meters are a necessity in any modern course in quantitative chemistry.

6. Related research.

Very few procedures in analytical chemistry are completely original. Usually such directions are developed and adapted by many teachers, control chemists, and researchers to suit their particular needs. Such has been the case in the development of the present manual of quantitative procedures. The authors have examined many recent monographs, research references, and textbooks in seeking out materials which might be adapted to their laboratory course. The authors have also consulted with teachers in other colleges and universities as to desirable features which should be incorporated into a course in elementary quantitative chemistry. Among the schools visited were the Medical College of Virginia, University of Virginia, Davidson College, University of North Carolina, Duke University, University of South Florida, Florida Presbyterian College, Dartmouth College and Amherst College.

7. Procedure.

Mimeographed directions for quantitative chemistry have been in use in our Chemistry Department during the past twenty years. These directions have been changed and modified greatly over this extensive period. In this project the authors have drastically revised these procedures and added others to bring the laboratory course abreast with modern trends. Suggestions from other teachers have influenced the inclusion of several methods and techniques.

The resulting procedures were used by students during the two semesters of the 1965-66 college term. During the trial period the laboratory directions were subjected to continuous change and revision in a search for the best possible methods. Suggestions from students were sought and included, where desirable in the present edition of the laboratory manual.

8. Analyses of the data and findings.

Results from analytical unknowns, which have been used for many years were compared with results secured from the present procedures.

The grading system given on page 25 of the manual has been used in the past, and was used during the present testing period. However, this system was modified for colorimetric procedures and potentiometric titrations, where attainable accuracy is less than for most standard quantitative procedures.

The procedures which have been developed in the present project have increased student accuracy to a decided degree as is evidenced by higher grades on the analyses of unknown samples. The degree of improvement cannot be evaluated precisely for many procedures, but in the case of colorimetric procedures, accuracy was increased approximately one hundred per cent. Perhaps even more important was the improvement in the speed of performing the analyses.

9. Conclusions and implications.

The new procedures have resulted in better grades for student analyses; they have also increased student efficiency in the performances of assigned laboratory tasks.

The use of simple instruments has given the students some familiarity with equipment, which may be of importance to them in their future professions. The authors intend to add other instruments, and instrumental procedures, to the laboratory course in the future when such usage appears feasible. A few additional existing instruments might be added now, but the authors believe that such instruments will become easier to use and cheaper in price within the foreseeable future. However, it is to be understood that the laboratory course, now and in the future, will not serve as a substitute for advanced courses in instrumental analysis.

10. Appendices, containing tables, instruments, and other materials.

These items are listed in detail within the appendix of the enclosed manual (five copies). The listings begin on page 112 of the manual, and it does not seem necessary to duplicate them under this heading.

SUMMARY

Title: THE DEVELOPMENT OF LABORATORY PROCEDURES FOR A COURSE IN ELEMENTARY QUANTITATIVE CHEMISTRY ON A FRESHMAN LEVEL WITH SOME EMPHASIS ON INSTRUMENTAL METHODS OF ANALYSIS:

Investigators:	Esmarch S. Gilreath	(Principal investigator)
	J. Brown Goehring	(Associate)
	William J. Watt	(Associate)

Institution: Washington and Lee University
Lexington, Virginia 24450

Project number: No. S-419-66

Duration: September 15, 1965 to August 15, 1966

5-8337

BACKGROUND

The majority of freshmen entering college have had some training in chemistry, and each year the preparation seems better. Much of the material traditionally included in introductory college chemistry courses is now being offered in many high schools and preparatory schools. It appears desirable to move more advanced introductory material into lower level courses in order to increase the scope and depth of more advanced courses. As general chemistry moves downward into the secondary schools it seems possible to transfer Quantitative Chemistry, which has customarily been a sophomore course, into the second semester of the freshman year. This change would permit the offering of organic and/or physical chemistry in the second year. The first semester of the freshman year might be devoted to a course in inorganic chemistry.

The rapid advances in chemical instrumentation are affecting curricular patterns as well as laboratory methods and techniques. Such instruments as electrical one-pan balances, pH meters, radio counters, simple photometers, and electric calculators are becoming standard pieces of equipment in the introductory courses. More advanced courses are feeling even greater effects from the advancing wave of chemical instrumentation. The present proposal is concerned with the development of laboratory procedures for elementary quantitative chemistry, with as much instrumentation as appears feasible, on a level of the college freshman year.

OBJECTIVES

The purposes for which the project was conducted are outlined in the following numbered fashion:

1. To move elementary quantitative chemistry from the sophomore year into the freshman year.
2. To make use of instrumental methods in quantitative analysis as far as is practical.
3. To design the experimental part of quantitative chemistry for the use of premedical students as well as other science students.
4. To bring the procedures of quantitative chemistry abreast with recent advances in chemistry.
5. To produce procedures which are as clear and complete as is possible.
6. To give explicit directions to teachers as to equipment, chemicals, and solutions needed in the laboratory procedures.
7. To offer, for teacher use, a time-tested method for grading student results in quantitative chemistry.
8. To describe quantitative techniques as they are needed within the procedures, and not lumped together in one chapter.
9. To integrate the use of instruments with classical quantitative techniques.

The objectives of the laboratory procedures are to provide disciplinal, educational, and practical values in the training of students. These objectives are listed as follows:

10. To give students an opportunity to use certain aspects of applied mathematics.
11. To instill a sense of objective honesty in the student in the evaluation of laboratory measurements.
12. To emphasize the value of neat and precise working habits.
13. To indicate the importance of recording laboratory data in a systematic form, and in a suitable notebook.
14. To familiarize the student with the literature of analytical chemistry.
15. To emphasize manipulative ability along with reasonable speed in the handling of chemical equipment.

OBJECTIVES (continued)

16. To bring an awareness on the part of the student as to the limitations of methods and equipment, and the magnitude of possible errors.
17. To train the student to make rapid calculations from analytical observations to a precision warranted by the data included.
18. To instill confidence in the student as to his ability to approach and solve laboratory problems.

PROCEDURE

Laboratory procedures for an elementary course in quantitative analysis, with some emphasis on instrumental methods, were developed in the following number fashion by the director of the project and his two associates:

1. The choice of materials resulted from a process of elimination. A broad list of topics was examined as to desirability, practicality, and educational value. The ones retained were those which appeared absolutely essential. These topics were used as headings for the five chapters of the laboratory manual, and are listed as follows:

Chapter 1	General Laboratory Directions
Chapter 2	Neutralization Methods
Chapter 3	Redox Methods
Chapter 4	Colorimetric Methods
Chapter 5	Precipitation Methods

2. Except for Chapter 1, all other chapters (topics) offered a variety of possible analytical determinations. Again, the choice of materials was reached by elimination. Only a limited amount of laboratory time is available within one semester, and only a limited number of analytical determinations can be performed by a group of students. However, it was felt that a number of optional experiments should be available, beyond a required number. These options would give a student a choice between certain determinations, and would permit a skillful analyst to obtain extra credit for additional work. Beyond the preliminary exercises, a student rarely completes more than eight determinations in one semester.

   The suggested schedule is as follows:

   Chapter 2. Two determinations required: Acid and Base

   Chapter 3. Four possible determinations, but only two required:
   Permanganate Processes: Iron or Calcium Carbonate
   Iodine Processes: Antimony or Copper

Chapter 4. Two possible determinations, but only one required:
Copper Oxide or Ferrous Ammonium Sulfate

Chapter 5. Four possible determinations, but only three required:
Option: Either Volumetric Chloride or Potentiometric Chloride
Required: Gravimetric Chloride, and Gravimetric Iron

3. Analytical results, except for the colorimetric determinations, were graded by the system which is outlined on page 20 in the laboratory manual. Since the unknown samples had been used in previous years, it was possible to compare results obtained with the new procedures with those obtained by older directions.

RESULTS

Major findings of the research:

1. Quantitative chemistry is a suitable course for the freshman college level. During the school term of 1965-66 the laboratory procedures of the project were used by sophomores in the fall semester, and by freshmen during the spring semester. No appreciable difference could be detected in the overall performance of the two groups.
2. A comparison of laboratory results with the new procedures for the session of 1965-66 with the old procedures used during the school term of 1964-65 revealed that the grades with the new procedures averaged six per cent higher than grades obtained with the older procedures.
3. A comparison of colorimetric determinations with the new procedures with those obtained in the past indicated an improvement in accuracy of approximately 100 per cent (twofold).
4. As indicated under PROCEDURES it was discovered that very few students could complete more than eight determinations (including preliminary exercises) during the course of one semester. The time involved was six hours per week for fifteen weeks (90 laboratory hours).
5. Instrumental determinations required less laboratory time, but more outside preparation than classical methods.
6. The accuracy obtained by classical methods of analysis was approximately three times that resulting from instrumental determinations. In other words, the accuracy of instrument was only one-third of that obtained by classical methods.

CONCLUSIONS

Major conclusions drawn from results obtained:

1. Elementary Quantitative Chemistry should be taught during the freshman college year, preferably in the second semester.
2. Well-worded laboratory procedures are rewarding to both students and teachers; better grades are obtained, and laboratory efficiency is increased.
3. Colorimetric procedures are not as accurate as classical methods. However, colorimetric methods are more rapid and are more adaptable to small percentages of constituents sought in analysis.
4. Eight analyses of unknown constituents make a desirable number for a one-semester laboratory course. This includes preparation and standardization of solutions, as well as other preliminary exercises.
5. It is desirable to include as many simple laboratory instruments as possible since familiarity with various instruments is becoming a necessity in all scientific fields.
6. Consultations with teachers in other colleges indicated the need to stress laboratory techniques and the use of instrumental methods. Also the student should be aware of the errors of analysis.

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PUBLICATIONS

Publications resulting from this project:

None.